JOURNAL

OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

1911. Vol. XCIX. Part II.

1224|2
15|5|12

LONDON:
GURNEY & JACKSON, 10, PATERNOSTER ROW.
1911.

Richard Clay & Sons, Limited,
Brunswick Street, Stamford Street, S.E.,
and Bungay, Suffolk.

CXLIII.—*The Alleged Complexity of Tellurium.*

By Augustus George Vernon Harcourt and Herbert Brereton Baker.

The anomalous position of tellurium in the periodic system has led to many attempts in recent years to separate it into elements of higher and lower atomic weights. Marckwald (*Ber.*, 1897, **40**, 4730), by a laborious process of fractional crystallisation of telluric acid, believed that he had obtained tellurium of atomic weight lower than that of iodine, but on repeating the atomic-weight determinations by a more trustworthy process he arrived at the conclusion that no separation had been effected (Marckwald and Foizik, *Ber.*, 1910, **43**, 1710). Baker and Bennett (Trans., 1897, **91**, 1849) described attempts at separation made by seven distinct methods, none of which afforded any evidence that the element was anything but simple. This conclusion was upheld by the work of Lenher (*J. Amer. Chem. Soc.*, 1899, **31**, 1).

More recently, however, Browning and Flint (*Amer. J. Sci.*, 1909, [iv], **28**, 347) asserted that if tellurium tetrachloride, dissolved in hydrochloric acid, is precipitated by a large excess of hot water, some separation of the element is effected. The work was continued by Flint (*Amer. J. Sci.*, 1910, [iv], **30**, 209). A large quantity of tellurium was purified by precipitation with sulphur dioxide, fusion of the precipitate with potassium cyanide, decomposition of the potassium telluride by air, and distillation of the product in a current of hydrogen. About 1000 grams of this material were converted into the dioxide, and dissolved in the minimum quantity of hydrochloric acid. This was poured into a large excess of boiling water, and allowed to remain. The dioxide which separated was again dissolved in hydrochloric acid, and precipitated by hot water. When this process had been repeated four times, atomic-weight determinations were made with the material, and gave a mean result of 126·59, and after ten repetitions of the same process the atomic weight obtained was only 124·32. No atomic-weight determinations are given in the paper of the less hydrolysable material.

Since this method of fractionation had been used by Baker and Bennett (*loc. cit.*) without success, and since the purification used by Flint was not unexceptionable, it was thought worth while to repeat the work. By the great kindness of Professor Marckwald, 200 grams of telluric acid, which had been recrystallised many times, were placed at our disposal for the purpose. It was not

thought necessary to purify the material further. The acid was boiled with hydrochloric acid until no further odour of chlorine could be observed. The solution of tellurium tetrachloride was evaporated, and dissolved in as small a quantity of hydrochloric acid as possible, the volume of the solution being 150 c.c. This was poured by degrees into 3650 c.c. of water, which was heated to the boiling point, the proportion of tellurium tetrachloride to water being the same as that employed by Flint. The precipitated oxide was dissolved in the minimum quantity of hydrochloric acid, and again partly precipitated by boiling water. The process was repeated until four fractionations had been performed. According to Flint, the dioxide last precipitated should contain tellurium with an atomic weight of nearly a whole unit lower than the accepted atomic weight.

In determining the atomic weight, a method was employed which had given very constant results in the hands of one of us, namely, the conversion of the element into the tetrabromide. To obtain the element, the dioxide was dissolved in hydrochloric acid, and the solution, after heating to the boiling point, was saturated with sulphur dioxide obtained from the liquefied gas. After remaining for a night, the precipitation was complete. The precipitate was washed with boiled distilled water until the washings gave no opalescence with barium chloride. After drying, the tellurium was melted in a current of hydrogen prepared by the electrolysis of purified barium hydroxide solution. The element prepared by this method was obtained in the form of an elongated button showing foliated crystallisation on the upper surface.

The method of determination of the atomic weight was precisely the same as that described in the previous paper. New platinum-plated weights were used, which were carefully standardised. The balance was an Oertling No. 5, which is only used for atomic-weight work. All the weights are calculated to vacuum standard.

The results of the determinations were:

	Weight of tellurium.	$TeBr_4$ formed.	Atomic weight.
1	0·87822	2·20103	127·55
2	0·59706	1·49640	127·55
3	0·69189	1·73442	127·53
4	0·62732	1·57254	127·53
5	0·58307	1·46162	127·53
		Mean	127·54

Determinations of the atomic weight of the material similarly purified, but without the attempted fractionation, gave a mean result of 127·53. Since no diminution was found in the atomic weight after four partial precipitations, a treatment which Flint had found to result in a diminution of nearly a whole unit in the

atomic weight, we considered it unnecessary to proceed further. It seems possible that the methods of purification used by Flint were insufficient to remove some element of lower equivalent than tellurium, and that this impurity accumulated when the process of fractionation was repeated.

In working up the residues for return to Professor Marckwald, two more precipitations of the tetrachloride by water were effected. In the last precipitation there was noticed a part of the precipitate which was orange in colour. On separation of this from the mass of white dioxide, it was proved to be tellurium trioxide, both by its giving off oxygen when heated alone, and by the evolution of chlorine on treatment with hydrochloric acid.

In order to see if this formation of trioxide afforded any help towards the explanation of Flint's results, some purified tellurium trioxide was treated with nitric acid, and the solution crystallised. The crystals were dried at 140°, and on decomposition gave a percentage loss of 17·35, the calculated loss for $2TeO_2,HNO_3$ being 16·49 (Te = 127·54). It thus appears that some formation of the higher nitrate takes place, and it is just possible that this may be the origin of the low atomic weights found by Flint. The atomic weight of the element, on the assumption that only $2TeO_2,HNO_3$ was present, deduced from this last experiment, would be 118·31. The formation of the trioxide, noted above, has been traced to the purified hydrochloric acid. It was inadvertently left exposed to the bright light prevalent during the last few weeks, and it was found to be seriously contaminated with chlorine.

We wish to express our thanks to Professor Marckwald for the loan of the highly purified telluric acid, and also to Dr. A. Scott for a supply of purified bromine.

CHRIST CHURCH, OXFORD.

CXLIV.—*The Solubility of Carbon Dioxide in Beer.*

By ALEXANDER FINDLAY and BUCCHOK SHEN, B.Sc., A.I.C.

THE importance of carbon dioxide for the sparkling quality and the palatability of beer, renders it somewhat remarkable that the solubility of this gas in beer has been studied so little. We have, indeed, found only two investigations of a quantitative character; and as a result of these, the view is most commonly held that beer

absorbs or dissolves more carbon dioxide than a corresponding solution of alcohol in water.

The most extensive and practically the only exact series of determinations of the carbon dioxide in beer are due to T. Langer and W. Schultze (*Zeitsch. für das ges. Brauwesen*, 1879, **2**, 369; 1883, **6**, 329). The values for the absorption coefficient of carbon dioxide in beer obtained by these investigators are given in table I, which we take from a paper by Emslander and Freundlich (*Zeitsch. physikal. Chem.*, 1904, **49**, 317).

TABLE I.

Temp.	Alcohol content in weight per cent.	Absorption coefficient of CO_2 in Beer.*	Alcohol solution.	Water.	Difference between columns 3 and 4.
0·6°	4·265	1·7625 (M)	1·64	1·7508	123 c.c.
1·0	2·996	1·8270 (A)	1·65	1·7207	177 ,,
1·1	4·303	1·7787 (M)	1·62	1·7133	159 ,,
1·4	4·341	1·7393 (M)	1·60	1·6913	139 ,,
2·6	3·022	1·6829 (A)	1·57	1·6060	113 ,,
2·7	4·381	1·7221 (M)	1·54	1·5991	182 ,,
2·8	2·709	1·6848 (A)	1·56	1·5923	125 ,,

* The letters M and A in this column refer to two different kinds of beer "Märzenbier" and "Abzugbier."

From these figures it would appear that beer absorbs or dissolves considerably more carbon dioxide than the corresponding water-alcohol solution, and even more than water itself. This increased absorptiou is attributed by Emslander and Freundlich, who discuss this question at length, to the presence in beer of positive colloids, and to the adsorption by these of carbon dioxide. The increased absorption they compare with the increase in the solubility of carbon dioxide in water in presence of ferric hydroxide (Geffcken, *Zeitsch. physikal. Chem.*, 1904, **49**, 257; Findlay and Creighton, Trans., 1910, **97**, 536).

The chief colloids present in beer are dextrin and albuminoids (in small amount), and the apparent increase in absorption is therefore attributed to these. Such an increase, however, is entirely opposed to the results obtained by Findlay and Creighton, who showed (*loc. cit.*) that the presence of dextrin not only does not increase the solubility of carbon dioxide in water, but, indeed, considerably diminishes it.

In view of the importance of a knowledge of the solubility of carbon dioxide in beer, and in view also of the apparent contradiction between the results obtained by Langer and Schultze and by Findlay and Creighton, we have thought it necessary to investigate

the matter more fully. We have therefore carried out a series of determinations of the solubility of carbon dioxide in solutions of ethyl alcohol in water, in wort, and in beers of different grades.

Experimental.

The method employed was the same as that described by Findlay and Creighton. Pure carbon dioxide, however, was used; it was prepared by the action of hydrochloric acid on pure marble. Its solubility in water at 25° was found to be 0·825.

Solubility of Carbon Dioxide in Solutions of Alcohol in Water at 25°.—It is known from the experiments of Müller (*Wied. Ann.*, 1889, **37**, 24) that the addition of alcohol (up to about 28 per cent.) lowers the solubility of carbon dioxide in water; but the actual solubility at 25° has not been determined. In table II therefore we give the results of our determinations at this temperature. The concentration of the solutions was obtained from determinations of the density and by interpolation from curves plotted according to the numbers given in the tables of Landolt-Börnstein-Meyerhoffer.

Table II.

Concentration: 2·95 grams of alcohol in 100 c.c.; $d_{15}^{25} = 0·99308$.

Pressure	737	836	929	1073	1213	1338
Solubility	0·812	0·813	0·812	0·811	0·813	0·811

Concentration: 3·01 grams of alcohol in 100 c.c.; $d_{15}^{25} = 0·99295$.

Pressure	745	823	937	1083	1226	1357
Solubility	0·814	0·812	0·815	0·813	0·812	0·812

Concentration: 8·83 grams of alcohol in 100 c.c.; $d_{15}^{25} = 0·98342$.

Pressure	747	846	942	1090	1231	1360
Solubility	0·786	0·786	0·784	0·785	0·786	0·788

Solubility of Carbon Dioxide in Wort.—The wort employed contained about 13 grams of solids in 100 c.c. In view of the changes which take place on keeping, the determinations of the solubility were carried out with the wort as soon as received. It was de-aerated by boiling under a pressure of 15 mm. of mercury. Table III gives the results of the determinations.

Table III.

Pressure	745	845	942	1092	1228	1360
Solubility	0·743	0·745	0·742	0·742	0·742	0·741
Pressure	755	856	955	1106	1250	1375
Solubility	0·741	0·743	0·742	0·739	0·738	0·738

Solubility of Carbon Dioxide in Beer.—The solubility was determined in three different grades of beer, the general composition of which is shown in table IV. The beer *C* was a strong beer.

TABLE IV.

	Grams per 100 c.c.		
	A.	*B.*	*C.*
Absolute alcohol	4·17	5·17	7·13
Maltose and other fermentable carbohydrates	1·09	1·45	5·57
Malto-dextrin	0·20	0·84	0·18
Free dextrin and other unfermentable matter	2·3	2·92	3·88
Total solids	4·32	6·10	11·10

Beer *A* corresponded with the wort employed in the previous determinations.

As the beer contains a certain amount of yeast, there is a continuous, slow formation of carbon dioxide in the liquid. Before determining the solubility, therefore, it was necessary, not only to de-aerate the beer, but also to destroy the yeast. The beer was therefore boiled for some time under a reflux condenser. It was then allowed to cool, and was de-aerated by placing it under a diminished pressure of about 15 mm. for two hours, the temperature being kept below 10° in order to reduce the loss of alcohol to a small amount. The results of the solubility determinations are given in table V. Since "absorption coefficients" are, perhaps, more readily understood than "solubility coefficients," we have also stated our results in that form.

TABLE V.

Beer A.

Pressure	749	849	944	1090	1227	1353
Solubility	0·785	0·785	0·787	0·786	0·786	0·787
Absorption coefficient	0·709	0·803	0·896	1·033	1·168	1·284
Pressure	752	852	949	1096	1234	1358
Solubility	0·786	0·788	0·788	0·789	0·788	0·788
Absorption coefficient	0·713	0·809	0·901	1·042	1·172	1·290

Beer B.

Pressure	750	849	946	1096	1233	1359
Solubility	0·759	0·760	0·760	0·760	0·758	0·763
Absorption coefficient	0·686	0·778	0·867	1·004	1·127	1·250
Pressure	756	858	957	1107	1248	1374
Solubility	0·759	0·759	0·761	0·761	0·759	0·761
Absorption coefficient	0·692	0·785	0·878	1·015	1·142	1·261

Beer C.

Pressure	766	871	972	1127	1264	1394
Solubility	0·718	0·722	0·723	0·722	0·723	0·725
Absorption coefficient	0·663	0·758	0·847	0·981	1·102	1·218
Pressure	763	867	968	1123	1260	1389
Solubility	0·714	0·717	0·718	0·717	0·719	0·719
Absorption coefficient	0·657	0·750	0·838	0·971	1·090	1·204

It may be remarked that absorption of carbon dioxide by beer *C* took place at a comparatively slow rate.

Discussion of Results.

From the preceding tables it will be obvious that the solubility of carbon dioxide in wort and in beer is considerably less than the solubility in water. Moreover, if we compare the solubility in beer with that in the corresponding alcohol-water solution, we also find that the solubility is diminished. This is shown in table VI.

TABLE VI.

Per cent. alcohol by weight.	Solubility coefficient of CO_2 in Beer.	Solubility coefficient of CO_2 in Alcohol solution.
4·17	0·787	0·806
5·17	0·759	0·801
7·13	0·716	0·793

That the solubility coefficient in beer diminishes more rapidly than that in the alcohol solution is to be accounted for by the fact that in the beers with the higher alcohol content there is also a larger amount of solid in solution, and these also exercise a lowering effect on the solubility.

The results exhibited in the preceding tables are entirely in harmony with those obtained by Findlay and Creighton (*loc. cit.*; *Biochem. J.*, 1910, **5**, 294), who pointed out that surface adsorption is not sufficient in itself to produce a marked increase in the solubility of a gas in water at atmospheric pressure; and that in the few cases in which an increased solubility was observed it seemed most suitable to attribute the effect, except in the case of charcoal and silicic acid, to chemical combination. The possibility of chemical combination in the cases now under discussion appears to be excluded; and the fact that the solubility is independent of the pressure is also in opposition to the assumption of colloidal adsorption (Findlay and Creighton, *loc. cit.*).

How, then, is the discrepancy between our results and those obtained by Langer and Schultze to be explained? An examination of the method of procedure adopted by these investigators points at once to the explanation. The method employed, a modification of that due to Schwackhöfer, was as follows: A flask of about 1 litre capacity was partly exhausted. It was then attached by means of rubber tubing to a tap inserted in the cask of beer to be investigated. The cask was situated in a cool cellar, and the bung-hole was open; 200—300 c.c. of beer were then drawn into the flask, and the barometric pressure and the temperature of the cellar were read at the same time. The amount of carbon

dioxide in the beer was determined by passing the gas evolved through potassium hydroxide.

Although we do not doubt that the amount of carbon dioxide *in* the beer was accurately determined by this method, we are convinced that the amount so determined does not represent the true solubility of carbon dioxide in beer under the conditions of pressure and temperature prevailing in the cellar; the beer, we believe, *was not merely saturated, but supersaturated.* This belief we shall now attempt to justify.

The phenomenon of gas evolution from solution presents a number of peculiarities, but has not yet been studied to any great extent.* It is, however, fairly well known, as a matter of everyday experience, that the rate at which a gas is given off from a supersaturated solution (as in the case of soda-water, beer, and other sparkling beverages) is very variable, and depends to a considerable extent on the nature of the liquid. From a few preliminary experiments carried out in this laboratory, it would appear that colloids diminish the rate of evolution of gas, so that the solution may remain supersaturated for a considerable period of time. This behaviour is very marked in the case of beer, and is clearly demonstrated by the following experiments, in which three different kinds of beer, purchased in bottle, were employed, namely, an "Export Beer," an "Extra Stout," and a "Pale Ale."

The bottle of beer was opened carefully without shaking, and was connected immediately either with a manometer or with a gas burette. From the increase of pressure shown by the manometer, or from the volume of gas given off, an indication was given of the rate of evolution of carbon dioxide from the particular beer. The experiments were carried out at room temperature.

(*a*) *Stout.*—The pressure rose gradually at a rate of about 1·3 mm. of mercury per minute. At the end of about two hours, the bottle was shaken, after which a considerably more rapid evolution of gas was observed: about 3—4 mm. increase of pressure per minute on the average. About twenty-four hours after the commencement of the experiment there still occurred a pressure increase of 126 mm. in ninety-eight minutes; and even after four days the pressure still increased, and the rate of evolution of the gas could be increased by shaking.

In the case of another sample of the same kind of beer, the bottle was connected with a gas burette. Without shaking, the gas was evolved at the rate of about 6 c.c. in the first ten minutes. As the evolution progressed, the rate diminished.

(*b*) *Export Beer.*—With this beer the rate of evolution of carbon

* The subject is under investigation in this laboratory.

dioxide was much slower. In about one hundred and fifty minutes the pressure increased to only 79 mm., and the volume of gas given off in the same time was only about 8 c.c. The beer also appeared to be supersaturated to a less extent than the stout.

(*c*) *Pale Ale.*—In this case the evolution of gas was greater than in either of the previous cases. In ten minutes about 14 c.c. of gas were evolved.

Although we do not claim any great accuracy for these experiments, they seem to show conclusively that considerable time is required for the equilibrium pressure to be established when no shaking occurs.

In the preparation of beer, whether during the primary fermentation or during the after-fermentation in the cask, carbon dioxide is formed in the body of the liquid. It has, however, been shown conclusively by Lamplough (*Proc. Camb. Phil. Soc.*, 1908, **14**, 580), in the case of the decomposition of diazo-salts in solution, that the liquid always becomes supersaturated with gas unless it is subjected to fairly vigorous shaking or stirring. We are therefore justified in assuming that during the fermentation in cask, where there is an absence of mechanical disturbance, the beer becomes supersaturated with carbon dioxide, the rate of escape of gas from solution being less than the rate of its formation. In the case of beer, also, it will probably be found that the evolution is retarded by the presence of colloids and other substances, so that supersaturation is facilitated. In the case of the experiments of Langer and Schultze, therefore, the barometric pressure cannot represent the saturation pressure of the carbon dioxide in the beer; and the amount of carbon dioxide which they found cannot represent the solubility of that gas in beer.

Since the temperature of the beer investigated by Langer and Schultze was only a few degrees above zero, it might be objected that at the much higher temperature employed by us the relationships might be reversed. We have, however, determined the solubility of carbon dioxide in water and in beer also at 12°, but do not find that this objection is a valid one. The solubility of carbon dioxide in water at 12° is 1·158; while the solubility in a beer containing about 4·6 per cent. of alcohol, and about 5 per cent. of solid matter, was 1·080.

If, then, we are right in the interpretation given above of the results obtained by Langer and Schultze, the explanation put forward by Emslander and Freundlich of the alleged increase of solubility of carbon dioxide in beer as compared with its solubility in a corresponding solution of alcohol in water is quite unnecessary, because no such increase is found. We are, however, not at all

unwilling to believe that the colloids present in beer play a very important part in the practical manufacture of a palatable beverage by facilitating the production to a greater or less extent of supersaturation, and, possibly, increasing the persistency of the "head." As previously indicated, however, the question is one which requires to be more fully investigated.

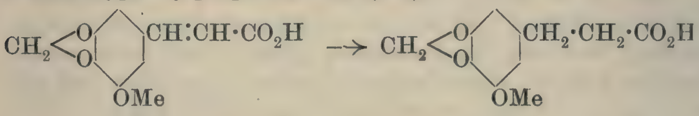
We are indebted to Professor A. J. Brown, F.R.S., for interest taken in this work.

UNIVERSITY OF BIRMINGHAM.

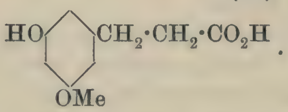
CXLV.—*Synthesis of* 4 : 6-*Dimethoxy*-2-β-*methylaminoethylbenzaldehyde.*

By ARTHUR HENRY SALWAY.

IN a previous communication (Trans., 1910, **97**, 2413) it was shown that 3-methoxy-4 : 5-methylenedioxycinnamic acid (I) is converted by the action of sodium amalgam into a mixture of β-3-methoxy-4 : 5-methylenedioxyphenylpropionic acid (II) and β-5-hydroxy-3-methoxyphenylpropionic acid (III):

 and

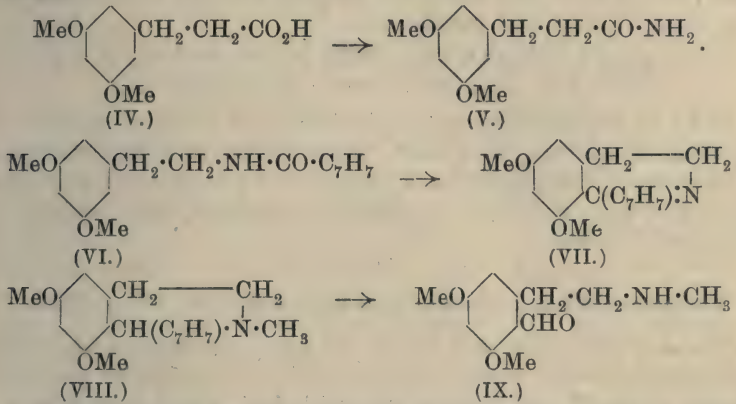
(I.) (II.)



(III.)

This reduction was originally conducted with the object of preparing β-3-methoxy-4 : 5-methylenedioxyphenylpropionic acid (II), from which the synthesis of cotarnine was accomplished by a series of reactions already described (Trans., 1910, **97**, 1208). It now seemed desirable to subject the second reduction product, β-5-hydroxy-3-methoxyphenylpropionic acid (III), to a similar series of reactions, since the final product thus obtained would be closely allied to cotarnine, and therefore likely to possess valuable therapeutic properties. Accordingly, β-5-hydroxy-3-methoxyphenylpropionic acid (III) was first methylated, and the resulting β-3 : 5-dimethoxyphenylpropionic acid (IV) transformed successively into

β-3 : 5-*dimethoxyphenylpropionamide* (V), *phenylacetyl*-β-3 : 5-*dimethoxyphenylethylamide* (VI), 6 : 8-*dimethoxy*-1-*benzyl*-3 : 4-*dihydroisoquinoline* (VII), 6 : 8-*dimethoxy*-1-*benzyl*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (VIII), and, finally, 4 : 6-*dimethoxy*-2-β-*methylaminoethylbenzaldehyde* (IX), according to the following scheme:



4 : 6-Dimethoxy-2-β-methylaminoethylbenzaldehyde (IX) is closely allied to cotarnine and hydrastinine, and is also isomeric with 4 : 5-dimethoxy-2-β-methylaminoethylbenzaldehyde, recently obtained by Pyman (Trans., 1909, **95**, 1266) by the oxidation of the alkaloid laudanosine. In view of the fact that each of these compounds possesses valuable therapeutic properties, a physiological examination of the synthetic 4 : 6-dimethoxy-2-β-methylaminoethylbenzaldehyde was desirable, and this has kindly been undertaken by Dr. P. P. Laidlaw, of the Wellcome Physiological Research Laboratories, to whom the author here wishes to express his best thanks. As a result of these experiments it has been shown that whilst the action of the substance on the isolated uterus closely resembles that of cotarnine and 4 : 5-dimethoxy-2-β-methylaminoethylbenzaldehyde, it is considerably less toxic than either of these compounds. When injected into the blood-stream of a cat it produces a rise in blood pressure, accompanied by a slowing of the heart-beat, in this respect having a closer resemblance to 4 : 5-dimethoxy-2-β-methylaminoethylbenzaldehyde than to cotarnine.

Experimental.

β-3 : 5-*Dimethoxyphenylpropionamide* (V, above).

This compound was prepared from β-3 : 5-dimethoxyphenylpropionic acid (Trans., 1910, **97**, 2417) by the successive action of phosphorus pentachloride and ammonia, the method employed being

the same as that already described in connexion with the preparation of β-3-methoxy-4:5-methylenedioxyphenylpropionamide (Trans., 1910, **97**, 1211). The crude acid amide was extracted with chloroform, and the chloroform solution washed with water, dried, and the solvent removed. The oily product thus obtained in almost quantitative yield soon solidified, and was purified by recrystallisation from benzene and petroleum:

0·0978 gave 0·2256 CO_2 and 0·0632 H_2O. C=62·9; H=7·2.

$C_{11}H_{15}O_3N$ requires C=63·2; H=7·2 per cent.

β-3:5-*Dimethoxyphenylpropionamide* is readily soluble in benzene, chloroform, or alcohol, but insoluble in light petroleum. It crystallises from a mixture of benzene and petroleum in colourless needles, melting at 80—81°. The fused substance, after resolidification, melts at 86°.

Phenylacetyl-β-3:5-*dimethoxyphenylethylamide* (VI, p. 1321).

The above-described acid amide was finely powdered, and shaken continuously with a slight excess of sodium hypochlorite (compare Trans., 1910, **97**, 1212) until the whole had passed into solution. The liquid was then heated to 100° for a short time, and, after cooling, thoroughly extracted with ether. The ethereal solution, which contained the β-3:5-dimethoxyphenylethylamine formed in the reaction, was agitated with small portions of dilute hydrochloric acid until no further quantity of base was extracted. The acid extracts were then united, and shaken with an excess of phenylacetyl chloride in the presence of alkali. The crude phenylacetyl derivative thus obtained did not solidify; it was therefore extracted with ether, the ethereal solution washed successively with dilute hydrochloric acid and water, then dried, and the solvent removed. The residue soon solidified, and was purified by crystallisation from dilute alcohol:

0·1104 gave 0·2918 CO_2 and 0·0701 H_2O. C=72·1; H=7·1.

$C_{18}H_{21}O_3N$ requires C=72·2; H=7·0 per cent.

Phenylacetyl-β-3:5-*dimethoxyphenylethylamide* crystallises from dilute alcohol in colourless, prismatic needles, melting at 73°. It is readily soluble in the usual organic solvents, except light petroleum.

In one experiment for the preparation of the above compound a considerable excess of sodium hypochlorite was used, which caused the reaction to take an abnormal course, as indicated by the formation of a phenylacetyl derivative, melting at 106°, instead of 73°. This product was found to contain chlorine, and gave, on analysis, the following result:

0·1050 gave 0·2498 CO_2 and 0·0575 H_2O. C=64·8; H=6·1.
0·2331 „ 0·0990 AgCl. Cl=10·5.

$C_{18}H_{20}O_3NCl$ requires C=64·8; H=6·0; Cl=10·6 per cent.

The chlorinated base corresponding with this phenylacetyl compound yielded a hydrochloride, which crystallised in radiating clusters of colourless needles, melting at 188°:

0·1096 gave 0·1930 CO_2 and 0·0618 H_2O. C=48·0; H=6·3.
0·1510 „ 0·0858 AgCl. Cl (as hydrochloride)=14·1.

$C_{10}H_{14}O_2NCl,HCl$ requires C=47·6; H=6·0;
Cl (as hydrochloride)=14·1 per cent.

It is thus evident that in the above experiment one atom of hydrogen had been substituted for one atom of chlorine, and since the chlorinated compound yielded, on oxidation, a monochlorodimethoxybenzoic acid (m. p. 181—182°) of the formula $C_9H_9O_4Cl$ (neutralisation value: Found: 254·6. Calc., 259·1), it follows that the chlorine must be present in the nucleus. The above compound, melting at 188°, is therefore the *hydrochloride of* β-2(4)-*chloro*-3 : 5-*dimethoxyphenylethylamine*.

6 : 8-*Dimethoxy*-1-*benzyl*-3 : 4-*dihydro*iso*quinoline* (VII, p. 1321).

A quantity (10 grams) of phenylacetyl-β-3 : 5-dimethoxyphenylethylamide was dissolved in xylene, the solution heated to boiling, and phosphoric oxide added in small quantities, with agitation, until a small portion of the xylene solution gave no precipitate of unchanged substance with light petroleum. The solvent was then decanted from the yellow mass of phosphorus compound, and the latter decomposed by warming with an excess of dilute hydrochloric acid. The acid liquid was filtered to remove a little resinous matter, then rendered alkaline, and extracted with ether. After washing with water, the ethereal solution was shaken with small portions of dilute hydrochloric acid until no further basic matter was removed. The extracts were then united, and concentrated to a small volume, when an almost colourless, crystalline hydrochloride was deposited, which was collected and purified by recrystallisation from a mixture of alcohol and ethyl acetate. The yield of pure substance amounted to 8 grams:

1·6464 lost, at 110°, 0·1678 H_2O. H_2O=10·2.

$C_{18}H_{20}O_2NCl,2H_2O$ requires H_2O=10·2 per cent.

0·1060 * gave 0·2652 CO_2 and 0·0643 H_2O. C=68·2; H=6·7.
0·4730 * „ 0·2140 AgCl. Cl=11·2.

$C_{18}H_{20}O_2NCl$ requires C=68·0; H=6·3; Cl=11·2 per cent.

6 : 8-*Dimethoxy*-1-*benzyl*-3 : 4-*dihydro*iso*quinoline hydrochloride* is

* Anhydrous substance.

only moderately soluble in cold water, but readily so in hot, and crystallises from the latter in almost colourless, rhombohedral prisms, which contain two molecules of water of crystallisation, and melt and decompose at 181°. It is best crystallised from a mixture of alcohol and ethyl acetate, when it is obtained in stout, colourless prisms. The free base, 6:8-*dimethoxy*-1-*benzyl*-3:4-*dihydro*iso*quinoline*, when prepared from the pure hydrochloride by addition of alkali, was obtained as a viscid oil, which did not solidify at the ordinary temperature. It yields a *picrate*, which is only moderately soluble in hot water, but readily so in alcohol, from which it crystallises in small, yellow prisms, melting at 184°.

6:8-*Dimethoxy*-1-*benzyl*-2-*methyl*-1:2:3:4-*tetrahydro*iso*quinoline* (VIII, p. 1321).

This compound was prepared by the conversion of 6:8-dimethoxy-1-benzyl-3:4-dihydro*iso*quinoline into its methochloride, and subsequent reduction with tin and hydrochloric acid, the method employed being identical with that previously described in the preparation of benzylhydrocotarnine from 8-methoxy-6:7-methylenedioxy-1-benzyl-3:4-dihydro*iso*quinoline (Trans., 1910, **97**, 1215). The crude product of the reaction was a brown oil, which slowly solidified. It was purified by recrystallisation from light petroleum, from which it separated in stout, colourless, prismatic needles:

0·0927 gave 0·2620 CO_2 and 0·0660 H_2O. C = 77·1; H = 7·9.

$C_{19}H_{23}O_2N$ requires C = 76·8; H = 7·7 per cent.

6:8-*Dimethoxy*-1-*benzyl*-2-*methyl*-1:2:3:4-*tetrahydro*iso*quinoline* is a crystalline, colourless solid, melting at 52°, and is readily soluble in organic solvents. It yields a *picrate*, which is only moderately soluble in hot water, but readily so in alcohol, and crystallises from the latter in small, feathery needles, melting and decomposing at 195°.

4:6-*Dimethoxy*-2-β-*methylaminoethylbenzaldehyde* (IX, p. 1321).

Five grams of 6:8-dimethoxy-1-benzyl-2-methyl-1:2:3:4-tetrahydro*iso*quinoline, dissolved in dilute sulphuric acid (15 per cent.), were oxidised by heating on the water-bath for about an hour with 4 grams of pyrolusite. An excess of sodium carbonate was then added, and the precipitated manganese carbonate removed by filtration. The filtrate contained, in suspension, some benzaldehyde formed during the oxidation, and was therefore extracted with ether, after which it was rendered strongly alkaline with aqueous sodium hydroxide, and the liberated base dissolved in benzene. The benzene extract was washed with a little water, and then shaken

with successive small portions of dilute hydrobromic acid until no further quantity of base was removed by this treatment. The aqueous solution of hydrobromide thus obtained was concentrated to dryness on the water-bath, and the solid residue purified by crystallisation from a mixture of alcohol and ethyl acetate:

0·2516 (air-dried) lost 0·0148 H_2O at 100°. $H_2O = 5·9$.

$C_{12}H_{16}O_2NBr,H_2O$ requires $H_2O = 5·9$ per cent.

0·1154 * gave 0·2138 CO_2 and 0·0608 H_2O. C = 50·5; H = 5·9.

0·2219 * „ 0·1444 AgBr. Br = 27·7.

$C_{12}H_{16}O_2NBr$ requires C = 50·3; H = 5·6; Br = 28·0 per cent.

4 : 6-*Dimethoxy-2-β-methylaminoethylbenzaldehyde hydrobromide* is readily soluble in alcohol or water, giving deep yellow solutions. It crystallises from a mixture of alcohol and ethyl acetate in pale yellow needles, which contain one molecule of water of crystallisation. The hydrated salt, when heated rapidly, melts at 100°, whilst the anhydrous substance melts without decomposition at 164°. The *hydrochloride*, owing to its hygroscopic nature, is more difficult to crystallise than the hydrobromide. It separates, however, from absolute alcohol and ethyl acetate in almost colourless, well-formed needles, which contain two molecules of water of crystallisation:

0·2437 (air-dried) lost 0·0304 H_2O at 90°. $H_2O = 12·5$.

$C_{12}H_{16}O_2NCl,2H_2O$ requires $H_2O = 13·0$ per cent.

The hydrated hydrochloride melts in its water of crystallisation at 95°. The free base, 4 : 6-*dimethoxy-2-β-methylaminoethylbenzaldehyde*, was obtained only in the form of a gummy solid on the addition of an excess of sodium hydroxide to a concentrated aqueous solution of the hydrobromide. It is freely soluble in water, but is reprecipitated on the addition of a concentrated aqueous solution of sodium hydroxide. It yields a *picrate*, which is readily soluble in hot water, and crystallises from this solvent in glistening, yellow needles, melting at 155—156°. The *aurichloride* crystallises from hot alcohol in golden-yellow leaflets, which melt at 131—132°:

0·0938 gave 0·0339 Au. Au = 36·1.

$C_{12}H_{16}O_2N,AuCl_4$ requires Au = 36·1 per cent.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

* Anhydrous substance.

CXLVI.—*Some New Inorganic Salts.*

By Thomas Vipond Barker.

The author's previous investigation of isomorphous groups of substances (Trans., 1906, **89**, 1120; *Min. Mag.*, 1907, **14**, 235; 1908, **15**, 42) shows that those members which approach each other nearly in molecular volume are capable of forming zone crystals or parallel growths on each other. For example, in the strictly isomorphous series consisting of potassium, rubidium, and cæsium sulphate the molecular volumes are respectively 65·3, 73·8, 85·2; the intermediate member, rubidium sulphate, is capable of forming parallel growths on crystals of either of the others, but the potassium and cæsium salts always give irregular deposits on each other. The remarkable crystallographic similarity which exists between the tetragonal mineral scheelite, $CaWO_4$, and the periodates of sodium and ammonium, led the author to the preparation of the periodates of potassium, rubidium, and cæsium (Trans., 1908, **93**, 15). The molecular volumes of these periodates are much greater than that of scheelite, and, in accordance with the author's theory, all attempts to obtain parallel growths of them on this mineral have proved fruitless. Since the molecular volumes of lithium salts are, as a rule, lower than those of the corresponding sodium compounds, it seems probable that the parallel growth would be observed if lithium periodate could be obtained. The author has therefore prepared the latter salt, but as it proves not to be isomorphous with the preceding series the fundamental condition necessary for the formation of a parallel growth is absent.

The double chromates of rubidium and cæsium with the metal magnesium, which have been prepared for the first time, present considerable chemical and crystallographic interest, for it has been found that the isomorphous relationship which exists between the simple chromates and sulphates also holds for the double salts of the formula $R_2Mg[(Cr,S)O_4)]_2,6H_2O$. The potassium salt is not comparable, as it crystallises with two molecules of water, but the ammonium salt described by Murmann (*Sitzungsber. K. Akad. Wiss. Wien.*, 1857, **27**, 175) and the rubidium and cæsium salts at present described, prove to be isomorphous with the well known series of double sulphates.

Lithium Periodate, $LiIO_4,H_2O$.—Rammelsberg (*Pogg. Ann.*, 1868, **134**, 389) prepared a basic salt, $Li_4I_2O_9,3H_2O$, and published satisfactory analytical data; in addition, he obtained from acid

solution another salt which he did not analyse, but from the fact of its being isomorphous with the sodium salt he assumed it to have the composition $LiIO_4$. The author has repeated Rammelsberg's work, and occasionally obtained crystals similar to those of Rammelsberg, but on analysis they invariably proved to consist of sodium periodate. If pure lithium carbonate and periodic acid are used, no tetragonal crystals are ever obtained; no matter whether the salt is crystallised from hot or cold solution, it is always hydrated, and, moreover, crystallises in the hexagonal system. The salt was prepared by dissolving slightly less than the theoretical quantity of lithium carbonate in a solution of periodic acid, and allowing to evaporate in a desiccator over sulphuric acid. The crystals which appear are simple hexagonal prisms; they are generally opaque in the centre, but clear at the edges, and are somewhat deliquescent. A measurement on the goniometer gave 60° angles in the prism zone. Viewed in the polarising microscope under crossed nicols, the crystals, which rest on the basal plane, remain dark on rotation, and in convergent light they exhibit a positive uniaxial figure central. The birefringence is medium. No pyramidal forms were ever observed, so that it was impossible to determine the ratio of the crystallographic axes $c:a$. Determinations of the iodine by the Carius method and of the water content were made:

0·3235 gave 0·3539 AgI. I = 59·14.
1·3484 (air-dried) lost 0·1159 at 200°. H_2O = 8·60.
$LiIO_4,H_2O$ requires I = 58·79; H_2O = 8·34 per cent.

Rubidium Magnesium Chromate, $Rb_2Mg(CrO_4)_2,6H_2O$.—This has not been described previously. It was prepared by mixing the proper quantities of solutions of rubidium chromate and magnesium chromate, the former itself being obtained by taking the correct quantities of rubidium hydroxide and chromic acid. Beautiful crystals are obtained by slow evaporation in the desiccator.

The analysis of the salt was kindly undertaken by Mr. H. E. Clarke, of Jesus College, and carried out as follows. A weighed amount of the salt was made up to a standard solution, and divided into two equal portions, one half being used for the magnesium determination by the ordinary phosphate method. The other half was used for the determination of the chromium and rubidium. The solution was reduced in acid solution by addition of ammonium bisulphite, the chromium precipitated as hydroxide, ignited, and weighed. The filtrate was evaporated to dryness, the ammonium salts volatilised, the magnesium removed by ammonium carbonate, and the rubidium ultimately determined as sulphate. The water

follows by difference. The results of two complete analyses are given in the following table:

	(1).	(2).	Mean.	Theory.
Rb_2O	35·05	34·94	35·00	34·89
MgO	7·62	7·62	7·62	7·54
CrO_3	37·38	37·54	37·46	37·39
H_2O by difference ...	—	—	19·92	20·18
			100·00	100·00

The percentage for a corresponding potassium salt would be $K_2O = 21·29$; $MgO = 9·11$; $CrO_3 = 45·19$; and $H_2O = 24·41$, so that the analytical results speak for a high degree of purity.

In all, six crystals were measured, five of them by Mr. R. C. Spiller and one by the author. The form and habit of the crystals are in all respects similar to those of the cæsium salt, a figure of which is given on p. 1329, but in addition to the forms there depicted small faces were sometimes found replacing the edge between the basal plane and the prism, and having the indices $\{111\}$ and $\{\bar{1}11\}$.

System: monoclinic. Ratio of the axes: $a:b:c = 0·7558:1:0·4950$; $\beta = 104°55'$. Following is a table of the results obtained by measurement of the two-circle goniometer, together with the corresponding values obtained by calculation.

		Mean observed.		Calculated.	
	No.	ϕ.	ρ.	ϕ.	ρ.
$m - 110$	12	53°51½′	—	—	—
$c - 001$	15	89 50	*14°55′	90°0	—
$r - \bar{2}01$	8	269 48	47 44	270 0	47°26½′
$q - 011$	18	27 54	*29 20½	28 17	—

Cleavage: moderately good parallel to $r - \{\bar{2}01\}$.

Caesium Magnesium Chromate, $Cs_2Mg(CrO_4)_2,6H_2O$.—The same method of preparation was employed as for the preceding salt, with which it is strictly isomorphous. In view of this it was only thought necessary to determine the water content:

0·8310 lost 0·1305 $H_2O = 15·7$.

$Cs_2Mg(CrO_4)_2,6H_2O$ requires $H_2O = 16·5$ per cent.

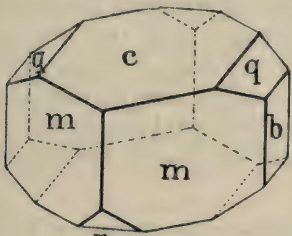
Well-defined crystals were obtained by slow evaporation over sulphuric acid; five of them were measured.

System: monoclinic. Ratio of the axes: $a:b:c = 0·7420:1:0·4886$; $\beta = 106°7'$. Forms: $m - \{110\}$, $c - \{001\}$, $b - \{010\}$, $q - \{011\}$, $r - \{\bar{2}01\}$, $o' - \{\bar{1}11\}$, and $o - \{111\}$. Out of thirty-five crystals examined with a lens, twenty-two had neither of the latter two forms, eleven had $\{\bar{1}11\}$, and only four had $\{111\}$. A typical crystal is shown in the figure.

Table of Measurements.

	No.	Mean observed. ϕ.	Mean observed. ρ.	Calculated. ϕ.	Calculated. ρ.
$b-010$	7	0°0′	90°0′	—	—
$m-110$	28	54 31	90 0	—	—
$c-001$	5	90 1	16 7	90°0′	—
$r-\bar{2}01$	9	270 0	47 28	270 0	47°15
$q-011$	9	30 33	29 35	30 36	—
$o-111$	2	63 10	47 17	63 22	47°28
$o'-\bar{1}11$	3	320 46	32 24	320 56	32 11

Cleavage: moderately good, parallel to $r-\{\bar{2}01\}$.



The author wishes to express his cordial thanks to Mr. H. E. Clarke for the very full analysis of the rubidium salt, also to Mr. R. C. Spiller, who carried out most of its angular measurements.

MINERALOGICAL DEPARTMENT,
UNIVERSITY MUSEUM, OXFORD.

CXLVII.—*The Action of Sodium Hypophosphite on Copper Sulphate in Aqueous Solution.*

By JAMES BRIERLEY FIRTH and JAMES ECKERSLEY MYERS.

THE action of sodium hypophosphite on copper sulphate in aqueous solution has been investigated to some extent by various workers, but there seems to be a diversity of opinion as to the exact nature of the product. It was with the object of arriving at some definite conclusion as to the course of the reaction that the present investigation was undertaken.

Wurtz (*Ann. Chem. Phys.*, 1844, [iii], **11**, 250) was of the opinion that in acid solution, or using hypophosphorous acid, the product was pure cuprous hydride (Cu_2H_2). Berthelot (*Compt. rend.*, 1879, **89**, 1005) doubted the existence of such a compound, and accord-

ingly repeated Wurtz's experiments. He obtained a substance which he considered might be regarded as a complex compound of hydroxide and phosphate of copper. In reply, Wurtz (*Compt. rend.*, 1879, **89**, 1066; 1880, **90**, 22) admitted the possibility of the presence of phosphate, but otherwise adhered to his original view. Berthelot's final statement on the matter was that the existence of cuprous hydride was purely hypothetical, since the substance contained constitutional water (*Compt. rend.*, 1879, **89**, 1097).

Experimental.

The present investigation is divided into two series of experiments: (1) Experiments carried out at the ordinary temperature; (2) Experiments carried out at higher temperatures.

Apparatus:—The reaction was carried out in all cases in an apparatus in which the precipitation, filtration, and drying are done in an atmosphere of carbon dioxide (Firth and Myers, Proc., 1911, **27**, 96).

Experiments at the Ordinary Temperature.

A concentrated solution of copper sulphate was prepared from the pure recrystallised salt, and to it was added a moderately concentrated solution of sodium hypophosphite,* the latter being in slight excess.

A white, flocculent precipitate appeared after a few minutes, which, on addition of a few drops of concentrated sulphuric acid, dissolved, giving a clear blue solution. On keeping, this solution underwent a series of changes. After five or ten minutes, the solution became green, and at the same time a granular, brick-red precipitate settled to the bottom of the tube. The solution was well stirred from time to time, and gradually darkened in colour, the precipitate assuming a reddish-brown, curdy appearance, and increasing in bulk. After about two hours the precipitate was still of the same colour, but a slow evolution of hydrogen commenced, and continued for about an hour. During its production the precipitate darkened, and finally, after the evolution had ceased, was almost black.

On removing the solution and precipitate from the reaction-tube, a film of copper was found on the sides of the vessel. When very thin, it appeared reddish-brown by reflected light and blue by transmitted light.

* The sodium hypophosphite was freshly prepared, and on treatment with barium nitrate in neutral solution gave only a slight opalescence, indicating that phosphate and phosphite were present only in traces.

From these observations it would appear that the action of sodium hypophosphite in acid solution is not a direct one, but proceeds through a series of stages. It was therefore considered necessary to examine as many of the stages as possible.

Examination of the Final Precipitate:—This precipitate was generally collected, after allowing the reaction to proceed over night. It was first thoroughly washed with water saturated with carbon dioxide, then with alcohol, followed by a mixture of alcohol and carbon disulphide. (If the latter is omitted, the precipitate contains free sulphur.) The carbon disulphide was removed by alcohol, and ether was passed through to dry the substance.

The precipitate obtained in this way was placed over calcium chloride in a desiccator, which was then evacuated. No appreciable decomposition of the substance was observed while it was in the desiccator. When thoroughly dry, the precipitate was quite black. Fifteen samples of this precipitate were examined, and it was found that oxygen, phosphate, hydrogen, and copper were invariably present. When quite dry the substance frequently decomposed suddenly on exposure to the air with the evolution of a considerable amount of heat. On one occasion a large desiccator, containing about ten grams of the substance, was shattered owing to the decomposition which was brought about by admitting a little air. Owing to this instability, the analysis of the substance was difficult, and samples were frequently lost when partly analysed.

In all cases the precipitate decomposed suddenly on applying the slightest heat, with the evolution of hydrogen and water-vapour, leaving a violet-coloured residue consisting of metallic copper, phosphate, and oxide. The analysis showed the following proportions:

$$Cu = 83{\cdot}6;\ O = 7{\cdot}6;\ P_2O_5 = 6{\cdot}4 \text{ per cent.}$$

When reduced in a stream of dry hydrogen, the residue consisted of metallic copper and phosphate:

$$Cu = 94{\cdot}8;\ P_2O_5 = 3{\cdot}8 \text{ per cent.}$$

All samples on keeping in moist air became light brown. Such a sample had the following composition:

$$Cu = 78{\cdot}8;\ O = 18{\cdot}6;\ P_2O_5 = 1{\cdot}9 \text{ per cent.}$$

On treatment with nitric acid the freshly prepared dry substance produces, first, hydrogen, and afterwards nitrous fumes.

The following table shows the percentage composition of various samples of the substance:

No.	Copper.	Oxygen.	P_2O_5.	Hydrogen.
1.	85·65	6·9	5·2	0·62
2.	82·5	9·73	5·4	0·46
3.	81·3	10·1	6·0	0·62
4.	84·58	8·68	4·7	0·59

Examination of the Intermediate Precipitates:—(*a*) The first precipitate, which was of a brick-red colour, was collected, washed, and dried as before. It was found to contain no hydrogen or phosphate, but only oxygen and copper, and analysis showed that it was almost entirely cuprous oxide. (Found, Cu = 89·6; O = 10·27. Calc., Cu = 88·7; O = 11·2 per cent.)

(*b*) The second stage was taken when the precipitate had darkened in colour and increased in bulk. Samples of this stage gave off hydrogen on heating slightly. The following values were obtained on analysis:

Cu = 88·5; O = 10·1; P_2O_5 = 0·74; H = 0·12 per cent.

Experiments at Higher Temperatures.

In this series of experiments the reacting substances were heated to various temperatures from 50° to 90° before mixing. The other details of experiment were the same as with the cold solutions, except that the desiccator in which the substance was kept was not evacuated, but only filled with carbon dioxide.

On mixing the solutions, a dark red precipitate was formed almost immediately, and hydrogen was rapidly evolved. As the precipitate increased in bulk the rate of evolution of the gas also increased. After a short time the precipitate clotted together, and darkened in colour.

On analysis it was found that oxide and phosphate were present in samples which had been prepared at temperatures either higher or lower than from 65° to 70°. It was also noticed that the same constituents appeared in specimens which had occupied more than a few minutes for their preparation.

The following analyses show the percentage composition of precipitates obtained after the reaction had proceeded for two minutes:

(*a*).	Cu = 98·6	H = 1·32
(*b*).	Cu = 98·2	H = 1·5
(*c*).	Cu = 98·4	H = 1·4

Cuprous hydride requires Cu = 98·45; H = 1·55 per cent.

The following values were obtained from samples occupying longer periods in their preparation. These specimens contained very little hydrogen:

Time.	Copper.	Oxygen.	P_2O_5.
45 mins.	91·6	7·0	0·66
70 ,,	85·7	12·3	1·44

The cuprous hydride prepared in this way is of a reddish-brown colour, and slowly decomposes in moist air at the ordinary temperature. It was therefore found necessary to make the analysis as

soon as the substance was dry. It decomposes suddenly at about 60°, with the evolution of hydrogen, leaving a sponge of metallic copper.

Conclusions.

In the cold the product of the reaction between an acidified solution of copper sulphate and a solution of sodium hypophosphite is a substance containing copper, hydrogen, phosphorus, and oxygen probably in the form of cuprous oxide, cuprous hydride, and copper phosphate. The instability of this substance is attributed to the co-existence of hydride and oxide. The same solutions at a temperature of about 70° interact with the production of cuprous hydride. In order to obtain this compound in a pure state, it is necessary to have the solutions moderately dilute, and to collect the precipitate within a few minutes of the mixing. When dry, the hydride is unstable, and cannot be kept for more than a day.

The difference between carrying out the reaction in the cold and at 70° appears to be that in the former case the production of oxide precedes that of hydride, whilst in the latter case the order is reversed.

THE CHEMICAL DEPARTMENT,
THE UNIVERSITY, MANCHESTER.

CXLVIII.—*Indicators of the Methyl-red Type.*

By HUBERT HOWARD and FRANK GEO. POPE.

METHYL-RED was first prepared by Rupp and Loose (*Ber.*, 1908, **41**, 3905), and it was suggested by them that it would be useful as an indicator in the titration of weak bases. Their method of preparation was not very satisfactory, and H. T. Tizard (Trans., 1910, **97**, 2485) gave a method of preparation by which almost quantitative yields were obtained. He also determined the strength of methyl-red as an acid and a base, and tested its value as an indicator, showing it to be greatly superior to methyl-orange. In his method of preparation, Tizard states that the alkali salts are very soluble, and that the potassium salt can only be obtained by evaporating an alcoholic solution to dryness, since it is soluble to a considerable extent in ether, and deliquescent in air. We have succeeded, however, in obtaining both the sodium and potassium salts in a crystalline condition, and although specimens of both salts have been kept

for some two or three months, neither as yet shows any signs of deliquescence.

The visible colour change when methyl-red is used as an indicator is from red to yellow, and the indicator can be used for very dilute solutions. We have prepared a number of other compounds of this type, using substituted amines, and find that very sensitive indicators are produced.

Experimental.

Methyl-red, $NMe_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}CO_2H$, was prepared by Tizard's method, and recrystallised from hot toluene, from which it separates in small prisms, melting at 183°, and closely resembling potassium permanganate in appearance. Apparently, no analysis of methyl-red, other than a nitrogen estimation, has been published; consequently, the following analysis was made:

0·1253 gave 0·3072 CO_2 and 0·063 H_2O. C = 66·87; H = 5·59.
0·1274 „ 17·2 c.c. N_2 (dry) at 23° and 750 mm. N = 15·36.
$C_{15}H_{15}O_2N_3$ requires C = 66·91; H = 5·58; N = 15·61 per cent.

The *sodium* salt was obtained by grinding 3 grams of methyl-red with 4 c.c. of a 10 per cent. solution of sodium hydroxide (a quantity of alkali, insufficient to convert the whole of the acid into salt). Bright scarlet plates were obtained in this way, and the whole mass was then allowed to remain in a vacuum over sulphuric acid until quite dry. The dry mass was then extracted with boiling toluene, filtered, the residue washed with hot toluene, and finally dried in a vacuum over sulphuric acid:

0·1476 gave 0·0356 Na_2SO_4. Na = 7·81.
$C_{15}H_{14}O_2N_3Na$ requires Na = 7·90 per cent.

The sodium salt crystallises in scarlet plates, and is readily soluble in water.

The *potassium* salt was prepared in a similar manner from 3 grams of the acid and 5·6 c.c. of a 10 per cent. solution of potassium hydroxide:

0·0992 gave 0·0284 K_2SO_4. K = 12·7.
$C_{15}H_{14}O_2N_3K$ requires K = 12·7 per cent.

The salt crystallises in dark red plates, is readily soluble in water, and by working with small quantities may be recovered from this solvent in a crystalline condition.

Attempts were made to prepare the ethyl ester of methyl-red, using Fischer and Speier's method, but the acid was recovered in an unaltered condition from the reaction mixture.

o-*Carboxybenzeneazodiphenylamine*,

$$CO_2H{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_5,$$

was prepared by combining diazotised anthranilic acid with the required amount of diphenylamine dissolved in about thirty times its weight of alcohol. The mixture was allowed to remain for two hours surrounded by ice, and was then heated on a water-bath to 40° for two hours, the precipitate collected, washed, dried, and crystallised from toluene:

0·1168 gave 0·3086 CO_2 and 0·0516 H_2O. C=72·06; H=4·91.
0·1904 „ 13 c.c. N_2 (dry) at 19° and 736 mm. N=13·45.
$C_{19}H_{15}O_2N_3$ requires C=71·93; H=4·73; N=13·25 per cent.

The acid crystallises from toluene in small, olive-green needles, showing a bronze reflex, and melts at 231°.

The *sodium* salt, as prepared by the method indicated above, crystallises in small, dark red needles, giving an orange-coloured solution in water:

0·1506 gave 0·0322 Na_2SO_4. Na=6·93.
$C_{19}H_{14}O_2N_3Na$ requires Na=6·78 per cent.

o-Carboxybenzeneazo-α-naphthylamine,
$CO_2H{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2$,
was prepared in an analogous manner by combining diazotised anthranilic acid with α-naphthylamine in alcoholic solution. The mixture was then allowed to remain for two hours in ice, and finally heated to 40° for two hours. The precipitated azo-compound was collected, washed, and recrystallised from alcohol:

0·1106 gave 0·2844 CO_2 and 0·041 H_2O. C=70·13; H=4·12.
0·1132 „ 14·3 c.c. N_2 (dry) at 23° and 750 mm. N=14·37.
$C_{17}H_{13}O_2N_3$ requires C=70·10; H=4·46; N=14·43 per cent.

The acid crystallises in minute, green prisms, which exhibit a metallic reflex, and melts at 243°.

The *sodium* salt crystallises in red needles, and gives a red solution in water:

0·1204 gave 0·0282 Na_2SO_4. Na=7·59.
$C_{17}H_{12}O_2N_3Na$ requires Na=7·35 per cent.

o-Carboxybenzeneazophenyl-α-naphthylamine,
$CO_2H{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NMe_2$,
was prepared similarly by combining diazotised anthranilic acid with dimethyl-α-naphthylamine in alcoholic solution. The precipitate was collected, washed, dried, and recrystallised from toluene:

0·1274 gave 0·3346 CO_2 and 0·0626 H_2O. C=71·63; H=5·46.
0·1114 „ 13 c.c. N_2 (dry) at 19° and 736 mm. N=13·21.
$C_{19}H_{17}O_2N_3$ requires C=71·47; H=5·33; N=13·16 per cent.

The acid crystallises from toluene in dark green needles, which melt at 196°.

The *sodium* salt is a dark reddish-brown solid, which is somewhat deliquescent:

0·226 gave 0·048 Na_2SO_4. Na = 6·88.

$C_{19}H_{16}O_2N_3Na$ requires Na = 6·75 per cent.

o-Carboxybenzeneazophenyl-α-naphthylamine,

$CO_2H{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_6H_5$,

was prepared in a similar manner, and crystallised from a mixture of alcohol and toluene:

0·1038 gave 0·2854 CO_2 and 0·042 H_2O. C = 74·99; H = 4·5.
0·1224 „ 12·43 c.c. N_2 (dry) at 19° and 736 mm. N = 11·80.

$C_{23}H_{17}O_2N_3$ requires C = 75·21; H = 4·63; N = 11·44 per cent.

The acid crystallises in green needles, which melt at 238°.

The *sodium* salt was obtained by dissolving the acid in hot alcohol, and adding the calculated amount of sodium carbonate dissolved in dilute alcohol. On concentration, the salt separates, and may be recrystallised from water, from which it separates in dark red needles:

0·1696 gave 0·0318 Na_2SO_4. Na = 6·07.

$C_{23}H_{16}O_2N_3Na$ requires Na = 5·91 per cent.

The following figures give some data obtained on titrating *N*/100-solutions of sodium hydroxide and sodium carbonate with acid, using the preceding azo-compounds as indicators. The indicator was used in the form of a cold saturated solution in alcohol (in which the azo-acid is only very slightly soluble), and two drops were added to 10 c.c. of the alkaline solution in each case. At these dilutions the end-point is quite sharply defined in all cases, much more so than when methyl-orange is used as indicator, and the colour change is more marked. Similar results were obtained in titrating *N*/100-solutions of ammonium hydroxide.

N/100.	Methyl-orange.	Methyl-red.	α-$C_{10}H_7{\cdot}NH_2$ derivative.	α-$C_{10}H_7{\cdot}NMe_2$ derivative.	$NHPh_2$ derivative.	$C_{10}H_7{\cdot}NHPh$ derivative.
			Volume of N/100-*Acid Required.*			
NaOH	10·3	10·0	10·0	10·0	10·0	9·95
Na_2CO_3 ...	10·22	10·0	10·0	10·0	10·0	10·0

In conclusion, we wish to tender our thanks to the Research Fund Committee of the East London College for a grant which has defrayed the expense of this investigation.

East London College,
University of London.

CXLIX.—*Dihydrocinnamenylcarbimide* (*β-Phenylethyl* iso*Cyanate*).

By Martin Onslow Forster and Hermann Stötter.

From the point of view of correlating structure and optical activity, it seemed desirable to compare a series of carbamates and carbamides derived from active alcohols and amines by interaction with the azides of dihydrocinnamic, cinnamic, and phenylpropiolic acids, when the products, having the general formulæ:

$$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}X,\ C_6H_5{\cdot}CH{:}CH{\cdot}NH{\cdot}CO{\cdot}X, \text{ and } C_6H_5{\cdot}C{\vdots}C{\cdot}NH{\cdot}CO{\cdot}X,$$

should illustrate the effect of ethenoid and acetylenoid linkings on specific rotatory power.

It has already been shown that such carbamates and carbamides arise from cinnamenylcarbimide (Trans., 1909, **95**, 433), although the action of this compound on menthol had not been studied, and we therefore prepared dihydrocinnamenylcarbimide from dihydrocinnamyl chloride and sodium azide in the expectation that its behaviour would be normal. That is, in fact, the case, and among the derivatives of β-phenylethylamine obtainable therefrom is menthyl dihydrocinnamenylcarbamate; but on attempting to prepare menthyl cinnamenylcarbamate, in order to compare its optical activity with that of the saturated compound, the only recognisable product was found to consist of menthyl carbamate, $C_{10}H_{19}{\cdot}O{\cdot}CO{\cdot}NH_2$, first described by Arth (*Ann. Chim. Phys.*, 1886, [vi], **7**, 464). Since the temperature at which the menthol and cinnamenylcarbimide were heated together was not much higher than that at which the latter had been rectified, it appears probable that the expected menthyl cinnamenylcarbamate breaks up at the moment of production into phenylacetylene and menthyl carbamate:

$$C_6H_5{\cdot}CH{:}CH{\cdot}NH{\cdot}CO{\cdot}OC_{10}H_{19} \longrightarrow C_6H_5{\cdot}C{\vdots}CH + NH_2{\cdot}CO{\cdot}OC_{10}H_{19}.$$

Although phenylacetylene could not be recognised, probably owing to polymerisation during the continued heating, and although methyl cinnamenylcarbamate could not be resolved into phenylacetylene and methyl carbamate, it is nevertheless noteworthy, as bearing on this transformation, that Thiele and Pickard, who first prepared methyl cinnamenylcarbamate (*Annalen*, 1899, **309**, 189), record the production of phenylacetaldehyde by the action of alcoholic potash on that substance, this change involving a disruption between carbon and nitrogen somewhat similar to that just mentioned.

In consequence of this unexpected obstacle and the subsequent

failure to convert phenylpropiolyl chloride into the azide, and therefrom generate the *iso*cyanate, the project outlined above has been abandoned.

Experimental.

Dihydrocinnamenylcarbimide (*β-Phenylethyl* iso*Cyanate*), $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}C{:}O$.

The dihydrocinnamyl chloride required for transformation into the azide was prepared by heating 40 grams of dihydrocinnamic acid with 35 grams of thionyl chloride during two hours on the water-bath; this procedure gave a quantitative yield of the chloride, which boiled at 133—135°/21 mm. Preliminary experiments showed that the interaction of the acid chloride and sodium azide is too sluggish at common temperatures to permit of the dihydrocinnamenylazoimide being isolated, and the higher temperatures at which the change does take place cause nitrogen to be liberated with production of the *iso*cyanate. Fifteen grams of dihydrocinnamyl chloride in 90 c.c. of dry toluene were heated with 7·5 grams of sodium azide during two days on an air-bath under reflux, moisture being excluded from the apparatus. The filtered liquid was then fractionated, and the portion boiling at 112—114°/15 mm. redistilled:

0·2490 gave 21·2 c.c. N_2 at 18° and 744 mm. N = 9·67.

C_9H_9ON requires N = 9·52 per cent.

The *iso*cyanate is a colourless, mobile liquid, boiling at 109—111°/13 mm., and having a faint, slightly pungent odour of cinnamon, whilst the carbimide character of the vapour becomes very pronounced in steam.

Derivatives of Dihydrocinnamenylcarbimide.

Dihydrocinnamenylphenylcarbamide,

$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_5$,

prepared from molecular proportions of the *iso*cyanate and aniline in dry ether, is moderately soluble in boiling alcohol, from which it crystallises in needles, melting to a turbid liquid somewhat indefinitely at 148°:

0·2393 gave 24·8 c.c. N_2 at 17° and 746 mm. N = 11·74.

$C_{15}H_{16}ON_2$ requires N = 11·67 per cent.

The anilide is sparingly soluble in hot benzene, from which it crystallises in lustrous leaflets; it is slightly soluble in boiling petroleum, and dissolves sparingly in boiling chloroform.

s-*Dihydrocinnamenylphenylsemicarbazide*,

$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}C_6H_5$,

separated immediately on mixing the *iso*cyanate with phenylhydrazine in dry benzene, and crystallises from boiling alcohol in lustrous needles, melting at 216°:

0·2145 gave 30·6 c.c. N_2 at 15° and 744 mm. N=16·27.

$C_{15}H_{17}ON_3$ requires N=16·47 per cent.

The substance is moderately soluble in boiling acetone, sparingly so in boiling benzene and chloroform, and insoluble in petroleum.

Menthyl dihydrocinnamenylcarbamate,

$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO_2{\cdot}C_{10}H_{19}$.

—Having ascertained that menthol is attacked only very slowly by the *iso*cyanate at the temperature of boiling benzene, 3·5 grams were heated with 3 grams of the carbimide during twenty hours at 130°, when the viscous product was submitted to a current of steam. Excess of menthol was quickly removed by this means, and on continuing the process during four days, when nothing further passed over, the residue was found to yield crystals on diluting its solution in alcohol with water. This product was twice recrystallised from dilute acetone, separating in silky needles, which melted at 86°:

0·1745 gave 0·4766 CO_2 and 0·1503 H_2O. C=74·49; H=9·63.

0·2163 „ 8·7 c.c. N_2 at 19° and 761 mm. N=4·64.

$C_{19}H_{29}O_2N$ requires C=75·25; H=9·54; N=4·62 per cent.

A solution containing 0·2500 gram, made up to 25 c.c. with absolute alcohol, gave α_D −1°57′ in a 3-dcm. tube, whence $[\alpha]_D$ −65·0°.

Interaction of Menthol and Cinnamenylcarbimide.

Cinnamenylcarbimide does not appear to act on menthol when the substances are dissolved in benzene, but on removing the solvent and heating the residue at 130° during two days, long, lustrous needles separated when the product cooled. By distillation in steam this material was carried over slowly, and after crystallisation from hot petroleum, melted at 162—163°, and gave $[\alpha]_D$ −81·6° in absolute alcohol (0·8 per cent.):

0·1069 gave 0·2601 CO_2 and 0·1032 H_2O. C=66·35; H=10·80.

0·2576 „ 16·2 c.c. N_2 at 21° and 778 mm. N=7·29.

$C_{11}H_{21}O_2N$ requires C=66·33; H=10·55; N=7·03 per cent.

As already explained, this product is not the menthyl cinnamenylcarbamate which might have been expected, but agrees in properties with menthyl carbamate, $C_{10}H_{19}{\cdot}O{\cdot}CO{\cdot}NH_2$, formation of which would involve elimination of phenylacetylene. In the hope of being able to recognise the latter, equivalent quantities of menthol and cinnamylazoimide were heated at the melting point

of the last-named until nitrogen ceased to be liberated, when the temperature was raised to 130°, and maintained at this point during six to eight hours; although lustrous needles sublimed in the cooler parts of the flask, showing that menthyl carbamate had been produced, phenylacetylene could not be recognised, either in the residue or in the small quantity of viscous material which condensed in the side-tube.

It was thought probable that phenylacetylene might be detected more easily if methyl cinnamenylcarbamate could be subjected to a similar change:

$$C_6H_5{\cdot}CH{:}CH{\cdot}NH{\cdot}CO_2{\cdot}CH_3 \longrightarrow C_6H_5{\cdot}C{:}CH + NH_2{\cdot}CO_2{\cdot}CH_3.$$

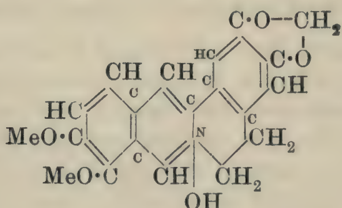
On heating the substance at 170° during six hours, however, the greater part of the material was recovered by steam distillation unchanged.

ROYAL COLLEGE OF SCIENCE, LONDON.
SOUTH KENSINGTON, S.W.

CL.—*The Constitution of Berberine.*

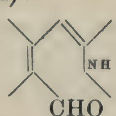
By CHARLES KENNETH TINKLER.

As the result of a long series of researches on berberine by Perkin (Trans., 1889, **55**, 63; 1890, **57**, 992; 1910, **97**, 321) and others, the constitution of the alkaloid is now represented by the formula (I):

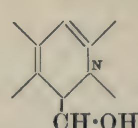


(I.)

It has, however, been pointed out by Gadamer (*Arch. Pharm.*, 1905, **243**, 31) that such a substituted ammonium hydroxide would also be capable of representation in the aldehydic (II) or carbinol form (III):



(II.)



(III.)

Perkin and Robinson (Trans., 1910, **97**, 321) state that the salts of berberine must be regarded as derived from the ammonium form of the substance, but the alkaloid itself exists in the corresponding aldehyde modification (II).

Gadamer (*loc. cit.*) has shown that two modifications of berberine can be obtained by the action of alkali hydroxides on the berberine salts. He supposes that berberinium hydroxide (I) is produced in solution by the addition of the calculated quantity of barium hydroxide to a solution of berberine sulphate. The other modification which he supposes is the aldehydic form of the substance (II), and which he has named berberinal, is obtained in the solid state by the addition of excess of sodium hydroxide to the aqueous solution of berberinium hydroxide. The aldehydic form of the alkaloid is the only form of the substance, according to Gadamer, which exists in the solid state. It thus appears that in the case of berberine a difficulty is met with in assigning one or other of the possible formulæ to the substance under various conditions.

In a paper recently published by A. Kaufmann and P. Strübin (*Ber.*, 1911, **44**, 680), purely chemical evidence is adduced in favour of the open-chain or aldehydeamine structure for the pseudo-bases, which have been investigated by Hantzsch, Decker, and others. In similar cases, however, of carbinol–ammonium base–aldehydeamine isomerism which have been investigated, it has been found impracticable to determine, on purely chemical grounds, which of the various possible formulæ should be assigned to a particular modification of a substance. In several cases important evidence has been obtained from a study of the physico-chemical properties of the substance.

Evidence in favour of the carbinol structure for cotarnine in the solid state and in certain solvents has been obtained from a study of the ultra-violet absorption spectra of the substance and its simple derivatives (Dobbie, Lauder, and Tinkler, Trans., 1903, **83**, 598). The evidence for the production of a carbinol from phenylmethylacridinium iodide by alkalis, originally demonstrated by Hantzsch (*Ber.*, 1899, **32**, 575) by means of conductivity experiments, has been supported by the absorption spectra method of investigation (Dobbie and Tinkler, Trans., 1905, **87**, 269; see, also, Dobbie and Tinkler, Trans., 1904, **85**, 1005; Tinkler, Trans., 1906, **89**, 856).

It may be pointed out that in addition to the physico-chemical evidence for the carbinol structure of these substances, chemical evidence is obtained by a study of the action of potassium cyanide on the substituted cyclic ammonium salts. In this case substances are obtained which are not true salts, but are generally regarded

as derived from the carbinol form of the hydroxide, that is, the cyanogen group of the true cyanide, like the hydroxyl group of the free ammonium base, is mobile.

In the present paper the results obtained by a spectroscopic examination of berberine and its simple derivatives are given. The object of the research was to obtain evidence as to the constitution of the alkaloid under various conditions.

Three derivatives of berberine—berberidic acid, berberine nitrate, and tetrahydroberberine—have previously been examined spectroscopically in showing the relation existing between corydaline and berberine (Dobbie and Lauder, Trans., 1903, **83**, 605). In connexion with the results of that investigation, Hartley (Kayser, *Handbuch der Spectroscopie*, 1905, **3**, 223) states that the second absorption band ($\lambda = 1/3000$) shown by dehydrocorydaline and berberine nitrates (1 milligram-molecule in 2500 c.c., 4 mm. to 1 mm.) belongs to the NO_3 group of the nitrate. This statement, however, has not been verified by the author. Not only do all the berberine salts and the free berberinium hydroxide show this same absorption band at this particular dilution, but nitric acid and nitrates, when examined at such dilutions and in layers of the same thickness as were employed in examining the berberine derivatives, show no absorption bands.

In connexion with the present investigation, the ultra-violet absorption spectra of the following substances have been examined: berberine and its chloride, sulphate, sulphite, and cyanide; methyldihydroberberine, berberinal, and the hydro-compound obtained in the decomposition of berberinal.

(*a*) *The Berberine Salts.*

The absorption spectra of berberine chloride, sulphate, and sulphite are almost identical with those of berberine nitrate as determined by Dobbie and Lauder (*loc. cit.*).

By the addition of a small quantity of an alkali hydroxide to the aqueous solution of the salts, no change in spectra is observed.

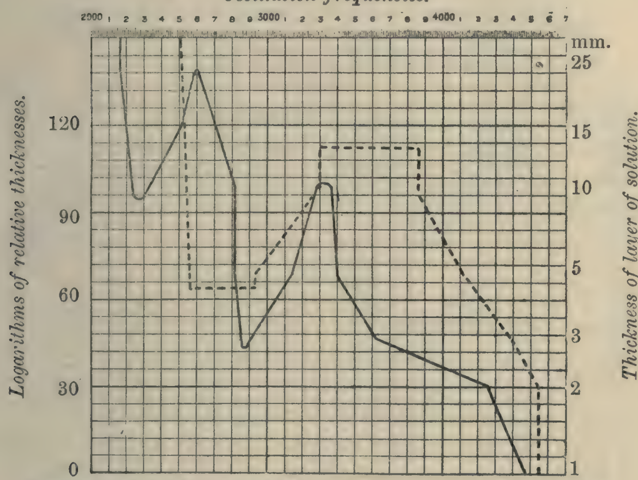
It is therefore concluded that berberinium hydroxide and the salts of berberine are constituted in the same manner (I), and that the salts are produced from the alkaloid by the loss of a molecule of water. The absorption curve for the berberine salts is represented in Fig. 1. The curve is drawn according to Baly's method, and so differs from that given by Dobbie and Lauder for berberine nitrate, in having oscillation frequency plotted against logarithms of relative thicknesses instead of actual thickness of layer of solution employed.

The addition of excess of a soluble base to the aqueous solution

of the salt, or the addition of a small quantity of soluble base to the alcoholic solution of the salt, causes a marked change in the absorption spectra of the solutions. In these spectra only one well-defined absorption band is given, whereas two absorption bands are observed in the spectra of the berberine salts. From the results obtained in other cases, it was expected that the carbinol form of berberine would be produced in these experiments. In order to verify the production of the carbinol, a simple derivative of this form of the alkaloid was sought, in order that its spectra might be compared with those of a solution of a berberine salt

FIG. 1.

Oscillation frequencies.



Berberine chloride in alcohol ————

Berberine chloride in alcohol containing caustic potash – – – –

1 *mg.-mol. in* 2500 *c.c.*

containing excess of alkali in the case of the aqueous solution, and a small quantity of alkali in the case of the alcoholic solution. For this purpose methyldihydroberberine (IV) was prepared by Freund and Beck's method (*Ber.*, 1904, **37**, 4677):

$$(MeO)_2C_6H_2<\begin{array}{l}CH{=\!=}C\text{———————}\\ CHMe\cdot \overset{|}{N}\cdot CH_2\cdot CH_2\end{array}>C_6H_2{:}O_2{:}CH_2.$$

(IV.)

There is apparently no doubt as to the constitution of this substance, and in it the linking of the carbon and nitrogen atoms is the same as that in the carbinol form of berberine (formula III).

The spectra of methyldihydroberberine and its salts agree closely with those of solutions of the berberine salts containing alkali, and

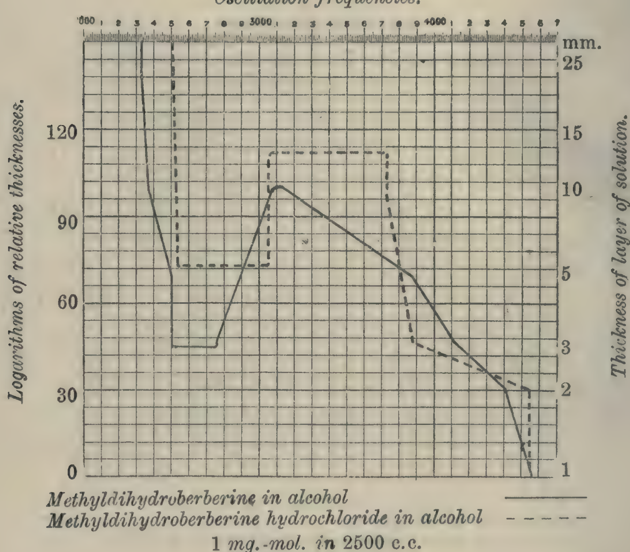
from this agreement evidence of the formation in these cases of the carbinol form of berberine is obtained.

The spectra of methyldihydroberberine and its salts are shown in Fig. 2, those of berberine chloride in alcohol containing a small quantity of alkali in Fig. 1 (dotted curve).

Evidence of the formation of the carbinol form of berberine in other cases is referred to under the spectra of berberine.

It appeared of interest to examine the spectra of berberine sulphite, as it is stated by Perkin (Trans., 1890, **57**, 1098) that

FIG. 2.



on account of its slight solubility, its constitution was for some time a matter of doubt.

The spectra of berberine sulphite in water and alcohol alone, and in these solvents containing sulphurous acid and sodium sulphite, are identical with each other and with those of the other berberine salts. No indication of the existence of a sulphite derived from the carbinol form of berberine was obtained.

As in the case of cotarnine, phenylmethylacridine, etc., the cyanide of berberine appears to be an abnormal salt, and from the results obtained in previous cases it was expected that berberine cyanide would be a pseudo-cyanide, derived from the carbinol form of the alkaloid (III). The absorption spectra of berberine cyanide in chloroform solution are in close agreement with those of methyl-

dihydroberberine, and are quite different from those of the true berberine salts. An aqueous or alcoholic solution of the cyanide, on the other hand, gives spectra which agree closely with those of the berberine salts. In aqueous solution the substance is probably hydrolysed; in alcohol it may be converted into a true cyanide. By the addition of potassium cyanide to the alcoholic solution of the substance, the spectra of the solution change to those characteristic of the linking in methyldihydroberberine.

The agreement of the spectra of berberine cyanide with those of methyldihydroberberine can only be explained by assigning to the former substance the constitution of cyanodihydroberberine (V):

$$(OMe)_2C_6H_2{<}\begin{matrix}CH{=\!=\!=}C{-\!-\!-\!-\!-\!-}\\ CH(CN){\cdot}N{\cdot}CH_2{\cdot}CH_2\end{matrix}{>}C_6H_2{:}O_2{:}CH_2.$$

(V.)

In addition to the agreement of the spectra of the solutions of methyldihydroberberine, cyanodihydroberberine, and the berberine salts in presence of alkali, these solutions resemble one another in the fact that, unlike the solutions of the berberine salts, they are all fluorescent.

(*b*) *Berberine.*

The free alkaloid is purified by crystallisation from water. Berberine prepared in this way is insoluble in ether, but chloroform, alcoholic, and aqueous solutions of the substance give spectra which are identical with those of the berberine salts. This agreement of the spectra of the solutions of the alkaloid with those of its salts would point to an ammonium base constitution for the solid substance, if the possibility of tautomeric change were excluded. From the results obtained in other cases, it would be expected that the substance would be stable in chloroform, but would assume the ammonium form in water or alcohol. It would therefore appear from the spectra of the chloroform solution that berberine crystallised from water has the ammonium base constitution in the solid state. Evidence in support of this is afforded by a spectroscopic examination of the other modification of the alkaloid, berberinal, which is soluble in ether (Gadamer, *loc. cit.*).

The representation of berberinal as an aldehyde (II) was supported by the formation of an unstable oxime from the substance (Gadamer, *Arch. Pharm.*, 1905, **243**, 31). This substance might, however, be represented as an α-substituted hydroxylamine, derived from the carbinol form of the base (III), as the evidence obtained from the spectroscopic examination of berberinal points to the fact that the substance is not the aldehydic, but the carbinol, form of

the alkaloid. The spectra of an ethereal * or chloroform solution of berberinal agree closely with those of methyldihydroberberine, and are identical with those of cyanodihydroberberine and an alcoholic solution of a berberine salt containing alkali. This agreement can only be explained by assigning to berberinal the carbinol formula (III), and the name *berberinol* is suggested for this substance.

Since solutions of both the carbinol and ammonium base forms of the substance are obtained by dissolving two different solids in the same solvent, chloroform, these solids must differ in constitution. Berberine crystallised from water is regarded as the ammonium form of the substance (I), and berberinol as the carbinol form (III). No evidence has yet been obtained, by this method of investigation, of the existence of the aldehydic form of the alkaloid (II).

The conversion of berberinol into berberinium hydroxide by means of excess of alcohol, or by solution in water, is readily followed by means of the spectroscope, an aqueous solution of berberinol giving spectra which are identical with those of the berberine salts. The reverse change, the conversion of berberinium hydroxide into berberinol, has been referred to under the berberine salts.

The decomposition of berberinal by the action of a concentrated solution of sodium hydroxide was investigated by Gadamer (*Arch. Pharm.*, 1905, **243**, 31). He supposed that simultaneous oxidation and reduction took place, as in the case of an aromatic aldehyde, with the production of a primary alcohol and an acid, the hydrated forms of dihydroberberine and oxyberberine respectively:

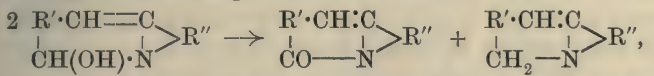
$$2\ \begin{array}{ll} R'\cdot CH{:}C & \!\!\!\text{---}R'' \\ | & \diagdown\diagup \\ CHO & NH \end{array} + H_2O \rightarrow \begin{array}{ll} R'\text{---}CH{:}C & \!\!\!\text{----}R'' \\ | & \diagdown\diagup \\ CH_2\boxed{OH\ H}N & \end{array} + \begin{array}{ll} R'\cdot CH{:}C & \!\!\!\text{---}R'' \\ | & \diagdown\diagup \\ CO\boxed{OH\ H}N & \end{array}$$

Recently Faltis (*Monatsh.*, 1910, **31**, 565) has suggested that the products of decomposition are oxyberberine and tetrahydroberberine; that is, that the decomposition is similar to that of methylquinoline-ψ-ammonium hydroxide, as suggested by Decker (*Ber.*, 1903, **36**, 2568), three molecules of the substance giving one molecule of the tetrahydro-derivative and two molecules of the oxy-derivative.

The spectra of solutions of the hydro-compound produced in the decomposition of berberinal by excess of sodium hydroxide are identical with those of methyldihydroberberine, and quite distinct

* Since berberinal can be recovered unchanged from ether, the spectra of the ethereal solution are regarded as the spectra of the solid substance.

from those of tetrahydroberberine. The decomposition of the substance can therefore be represented as follows:



two molecules of the carbinol giving one molecule of the oxy-compound and one molecule of the dihydro-compound.

Some of the materials used in this investigation have been purchased by means of a grant from the Research Fund of the Chemical Society, for which the author wishes to express his thanks.

THE UNIVERSITY,
BIRMINGHAM.

CLI.—*Cupriglycollates.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

IN a recent communication (this vol., p. 169) it was shown that those cupri-compounds which are formed by the action of alkalis on copper salts must be regarded as resulting from the addition of CuO to the molecule, and not from the substitution of atoms of copper for hydrogen atoms, either in the alcoholic hydroxyl or in the carboxyl groups. With alcoholic hydroxyl, the addition of CuO may be regarded as a displacement of H by CuOH; in the case of the copper being in the carboxylic portion of the molecule, the presence of $(Cu^{IV}O)''$ was suggested. The evidence depended on determinations of the minimum molecular weights of six different cupri-compounds of tartaric, saccharic and mucic acids. More positive evidence on this point would, however, be forthcoming if a cupri-salt of a monohydroxy-acid were obtainable, especially if the acid were also monobasic, for the atomic ratio of copper to (say) the potassium present in the potassium salt would then be 1:1, whereas on the theory of the copper displacing the hydrogen of the alcoholic hydroxyl it must be 1:2; thus:

$$RCH_2O(CuOH)CO_2K \quad \text{and} \quad \begin{matrix} RCH_2O \\ RCH_2O \end{matrix}\!\!>\!Cu\!\begin{matrix} CO_2K \\ CO_2K \end{matrix}.$$

Although such acids yield cupri-salts, it appears to be difficult to obtain them in a definite form: this has been noticed already as regards the quinic acid derivatives (*loc. cit.*, p. 178), and similar difficulties have been found with those of citric, lactic, malic and salicylic acids. Glycollic acid, however, has yielded better results,

and has also supplied another cupri-salt, which is of considerable importance in its bearing on the nature of these compounds.

Copper glycollate may be prepared by double decomposition, or by dissolving copper carbonate in the acid, forming, in either case, small, light blue crystals, which dissolve in water to the extent of 0·1 per cent. Cu at 10°, and 0·46 per cent. at 90°, the solution being quite stable on boiling.

When potassium hydroxide solution (0·04 per cent.) is added to a cold saturated solution of the salt, a light blue, flocculent precipitate of basic copper glycollate begins to form after a certain amount of alkali has been added (about 0·67 KOH for each Cu), and the liquid becomes alkaline when 1·64 K for each Cu has been added: 6·2 per cent. of the total copper remains in solution.

If the potassium hydroxide solution is added to the solid copper glycollate, the same proportion (1·61 KOH) is required to produce alkalinity, but the whole of the copper remains in solution, apparently in a colloidal condition; for the solution is opalescent, and can rarely be filtered. On the one occasion when it was successfully filtered, no trace of precipitate was left on the filter. If rather more water is present when the alkali is added, the whole liquid gelatinises.

When to the barely alkaline liquid obtained as above, excess of alcohol is added, a light blue, flocculent precipitate is formed, which consists of an imperfect emulsion. If this is filtered off rapidly (which is not always possible, owing to the emulsion de-emulsifying, and blocking the filter), it may be dried in a vacuum, and then at 140°. At 100° it is not quite anhydrous; and above 140° it begins to decompose.

It forms a light blue neutral powder, decomposed by water. Analyses of four preparations of it dried at this temperature gave:

	Cu.	K.	Ratio.
	30·59	18·39	1 : 0·98
	30·63	16·63	1 : 0·88
	30·99	18·03	1 : 0·95
	30·14	17·45	1 : 0·94
Mean	30·59	17·63	1 : 0·94
Theory for $CH_2O(CuOH)CO_2K,H_2O$	30·03	18·47	1 : 1

Considering that no method of purification is available, these values agree as nearly as can be expected with the formula given, and are conclusive against the ratio of copper to potassium being 1 : 2, as required on the view that the copper displaces an equivalent of hydrogen. The ratio in every case is rather more than 1 : 1, the potassium being displaced to a certain extent through

the action of water by some copper, as occurs in the case of all the cupri-compounds hitherto investigated.

The formula, as will be seen, represents a molecule of water as being present, and, since that cannot be eliminated without involving decomposition, the compound is probably an hydrol, containing the group $C(OH)_2OK$.

γ-Cupriglycollates.—The transformation of an ordinary copper salts containing $(CO_2)_2Cu''$ into a β-cupri-salt containing $\begin{matrix} C{\substack{OH \\ OK}} \\ | \\ CO_2Cu^{IV}O \end{matrix}$, has been represented as due, in part, to the tendency of the carbon atom to unite with OH and OK; and it was suggested that in the deep violet-blue liquids produced by the action of excess of alkali, which act on cellulose, this process has been carried a step further, the quadrivalent copper atom having, like the carbon atom, attracted to itself OH and OK, forming a cuprite group. These were termed γ-compounds. Attempts to isolate them in various cases were unsuccessful, but the ultimate product of the action of lime on copper sulphate is a substance showing the same colour and reactions as the γ-cupri-compounds, and, in its case, there must be a cuprite group present, for its formula is CuO(CaO) (Trans., 1907, **91**, 1995; 1910, **97**, 1858). In the case of the glycollate, the γ-cupri-salt has now been isolated.

In the preparation of the cupriglycollate already described, the addition of alcohol leaves from 3 to 12 per cent. of the total copper in solution, and after some time this separates in the form of violet crystals (hence the necessity, mentioned above, for filtering off the emulsion as rapidly as possible): these crystals may, however, be obtained in larger quantities by treating the solid glycollate with excess of potassium hydroxide before adding the alcohol: the excess of alkali, unless very considerable, causes a precipitation of basic copper glycollate, leaving about 40 per cent. of the total copper in solution, and the addition of alcohol then precipitates no emulsion, but a gradual separation of the above-mentioned violet crystals takes place. These appear to be of considerable size, but are found to be made up of bundles of soft, hair-like crystals: they are easily washed with alcohol, and, when dried, are of a mauve colour, unlike any ordinary copper salt. With water they give a strongly alkaline reaction, and are decomposed into a basic salt: in ordinary moist air they absorb carbon dioxide. They continue to be deposited from the alcoholic liquid during some forty-eight hours, only traces of copper remaining in solution, and the first and last crops give the same values on analysis. They suffer no change at 100°, but at 135° they lose water, and become lavender-

blue, decomposing at a higher temperature. The blue product on exposure to air gradually absorbs water, and becomes mauve again.

The proportions of alkali used were varied from 2 KOH to 10 KOH for each Cu present, the only difference noticeable under such variation being that with the higher proportions the amount of basic glycollate precipitated was considerably reduced, and the crystals were larger and more like tables than needles. Five preparations, of which No. V was obtained with 10 KOH, gave the following values: (No. I was of doubtful purity, and has been excluded from the mean):

	Cu.	K.	H_2O.	Ratio.
I.	(18·26	24·97	10·11	1 : 2·22 : 1·97)
II.	18·96	23·61	10·83	1 : 2·02 : 2·02
III.	19·47	22·69	10·56	1 : 1·90 : 1·91
IV.	19·19	23·20	10·79	1 : 1·97 : 1·98
V.	19·09	23·83	(6·37)	1 : 2·03 : (1·18)
Mean	19·20	23·33	10·73	1 : 1·98 : 1·97
Calculated	19·51	24·00	11·05	1 : 2·00 : 2·00

The calculated values may be deduced from compounds represented by:

$$(CH_2O)_2CuCO_2K_2,2H_2O \quad \text{or} \quad \begin{array}{l} HO{\cdot}CH_2{\cdot}C\begin{smallmatrix}OK\\OH\end{smallmatrix} \\ \qquad\qquad\quad | \\ HO{\cdot}CH_2{\cdot}CO_2Cu^{IV}\begin{smallmatrix}OH\\OK\end{smallmatrix} \end{array}$$

(I.) (II.)

The former agrees with the amount of water lost on heating in most cases, but must be rejected on account of the substance being strongly alkaline, which property is accounted for by the γ-cupriglycollate formula, II, although the loss of the elements of $2H_2O$ by such a substance can only be explained by its becoming transformed into the anhydrous form of No. I: a view which admits of the existence of cupri-salts formed by the substitution of copper for the hydrogen in alcoholic hydroxyl groups, although these may not be obtainable by the direct action of an alkali on copper salts. A change of this sort is of a somewhat profound character, but it is in accordance with the dehydration being accompanied by a loss of the characteristic mauve colour. It is also noticeable that in the case of preparation V, where the crystal appeared somewhat different in form, only half this amount of water was lost before decomposition began. A substance represented by formula II could lose $1H_2O$ with little alteration in structure.

The hydroxides of the other alkali metals behave similarly to that of potassium, certain gradational differences being observable throughout the series. The equivalents required to produce alkalinity are: 1·5 M′OH with lithium, 1·64 with sodium and potassium (and also with barium), 1·67 with rubidium, and 1·77

with cæsium. In all cases, the barely alkaline liquids are opalescent and unfilterable, excess of alkali producing a precipitate of basic salt, and the liquid becoming filterable. The γ-cupri-salts are thrown down on the addition of alcohol with greater difficulty as the atomic weight increases: the sodium salt is precipitated at once, the potassium salt begins to form in a few minutes, the rubidium salt forms much more slowly, and the yield is a very poor one, whilst the cæsium salt is not thrown down at all. The further addition of ether in this case causes the separation of a few drops of deep blue liquid, which apparently contain the γ-compound, but mixed with a large excess of cæsium hydroxide.

The rubidium salt is very similar to the potassium compound, but it forms larger crystals, and these are of a somewhat darker mauve colour. On heating, it gives off $1H_2O$ at 140°, like the preparation V of the potassium salt, and decomposes at 150°. On analysis, after drying at 100°, it gave:

	Cu.	Rb.	H_2O.	Ratio.
	15·01	40·48	4·24	1 : 2·01 : 1·0
Calculated	15·19	40·83	4·31	1 : 2·00 : 1·0

The sodium salt differs from the others in forming much finer, less-defined crystals, and in being violet, instead of mauve, on drying. Its composition, also, does not appear to be so simple as in other cases. Four preparations, obtained under different conditions, gave:

	Cu.	Na.	H_2O.	Ratio.
	21·61	16·37	(10·72)	1 : 2·09 : (1·73)
	21·38	17·22	7·45	1 : 2·23 : 1·23
	21·51	16·61	7·02	1 : 2·18 : 1·15
	21·75	16·88	7·32	1 : 2·15 : 1·19
Mean	21·56	16·77	7·29	1 : 2·16 : 1·19

In the case of lithium, no similar compound was obtained, the addition of alcohol causing only a very small precipitation of an amorphous solid.

Barium probably forms a γ-cupriglycollate, but the violet substance obtained was mixed with excess of barium hydroxide precipitated by the alcohol.

No indications of the formation of a calcium compound were obtained.

It is not improbable that the alkaline cupricitrate discovered by Luff has the same constitution as that suggested for the γ-cupriglycollates, instead of that previously suggested by the present author (Trans., 1910, **97**, 1844), for one of the conclusions drawn respecting it requires correction. It was found that its alkalinity was equivalent to one-sixth of the potassium present, and it was concluded, therefore, that one of the six potassium atoms was in

the "alkaline" condition. It seems impossible, however, to determine the actual number of atoms which are present in this condition, for, when the compound is decomposed, part of the potassium hydroxide liberated may produce an equivalent of copper oxide, forming a basic salt, or a neutral cupri-salt. The potassium γ-cupriglycollate, for instance, shows an alkalinity, when neutralised by acid, of only 0·3 K, a basic salt being precipitated. Luff's salt may, therefore, easily contain two atoms of "alkaline" potassium, and be represented by:

$$\begin{array}{l} \mathrm{C_6H_5O}^{\mathrm{(CO_2K)_2}}\;\mathrm{C}^{\mathrm{OK}}_{\mathrm{OH}} \\ \qquad\qquad\quad | \\ \mathrm{C_6H_5O}^{\mathrm{CO_2}}_{\mathrm{(CO_2K)_2}}\mathrm{Cu^{IV}}{}^{\mathrm{OH}}_{\mathrm{OK}} \end{array} \quad + \; 4\mathrm{H_2O}.$$

It presents the same difficulty as the γ-cupriglycollate, in losing $6H_2O$ when heated, as if it were $(C_3H_4O)_2Cu(CO_2K)_6,6H_2O$ (copper displacing hydrogen in hydroxyl), although such a formula is inconsistent with its alkalinity. Luff's salt forms large, violet-blue crystals, unlike those of the potassium and rubidium cupriglycollates, but this difference may be due to the presence of water of crystallisation, for the colour of the crystals is similar to that of the γ-cupriglycollates when in solution, or even when moist.

Basic Glycollates.—The proportion of 1·64 KOH to each molecule of copper glycollate in weak solution necessary to produce alkalinity would indicate—if all the copper were precipitated, as was nearly the case—the formation of a basic glycollate approximating $(C_2H_3O_3)_2Cu,5CuO$, and such was found to be the composition of the precipitate obtained, with $5H_2O$ retained at 100° and almost eliminated at 145°. (Found, Cu = 54·54; H_2O = 11·15. Calc., Cu = 54·37; H_2O = 12·84 per cent.) It is a bulky, fairly dark blue precipitate, which must be dried in a vacuum before being heated at 100°, or it partly decomposes, and also forms carbonate. In some other experiments in which a smaller proportion of alkali was added, and in which less water was present, two other basic salts were repeatedly obtained, one as a light blue, opaque precipitate, the other much darker and more transparent in appearance. Both of these suffered no decomposition on drying at 100°, and both became anhydrous at 145—160°. The former consisted of $(C_2H_3O_3)_2Cu,2CuO,H_2O$ (Found, Cu = 48·90; H_2O = 4·79. Calc., Cu = 48·80; H_2O = 4·61 per cent.), the latter of

$$(C_2H_3O_3)_2Cu,4CuO,2H_2O.$$

(Found, Cu = 56·78; H_2O = 6·25. Calc., Cu = 55·97; H_2O = 6·35 per cent.)

A cupriglycollate of the formula $(C_2H_3O_3)_7Cu_4K$, obtained by the

action of copper acetate on potassium glycollate, has been mentioned previously (this vol., p. 810), but its constitution has not been investigated.

The author takes the present opportunity of expressing his acknowledgment of assistance obtained from the Research Fund of the Chemical Society in his investigation of copper compounds.

HARPENDEN.

CLII.—*The Synthesis of Derivatives of Thioxanthone from Aromatic Disulphides.*

By EFFIE GWENDOLINE MARSDEN and SAMUEL SMILES.

IN a previous paper (Prescott and Smiles, this vol., p. 640) it was shown that aromatic disulphides are decomposed by concentrated sulphuric acid into a sulphoxylic acid and a mercaptan:

$$\mathrm{ArS{\cdot}SAr + H_2O \rightleftharpoons ArSOH + ArSH},$$

and further reasons were given for supposing that this reaction is reversible, the equilibrium in ordinary cases being greatly in favour of the disulphide. When, however, a suitable aromatic compound is added to the mixture, the sulphoxylic acid, being then converted into an unsymmetrical monosulphide, is removed, and the equilibrium is disturbed:

$$\mathrm{ArS{\cdot}OH + HAr = ArSAr + H_2O}.$$

If a sufficient quantity of the aromatic derivative is present, the disulphide may be completely converted into monosulphide. Meanwhile, the mercaptan, which now appears in excess, is oxidised by the sulphuric acid (Stenhouse, *Annalen*, 1861, **149**, 250) to the original disulphide, which becomes available for renewed decomposition. The complete process may thus be represented as follows:

$$\mathrm{ArS{\cdot}SAr + 2HAr + O = 2ArSAr + H_2O}.$$

When di-*o*-thiobenzoic acid was condensed with benzene in this manner it was found that thioxanthone was obtained; this substance is evidently formed by elimination of water from the unsymmetrical monosulphide, *o*-phenylthiolbenzoic acid:

$$\mathrm{CO_2H{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_5 = C_6H_4{<}{}^{CO}_{S}{>}C_6H_4 + H_2O},$$

which is produced in the first phase of the interaction.

In the present paper it is shown that this method may be applied to the synthesis of more complex derivatives of varied character.

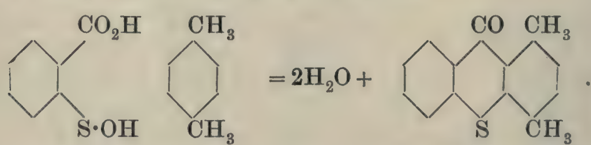
Generally speaking, the methods of synthesising thioxanthones from disulphides may be said to fall under either of two types:

(1) In one of these the carboxyl group which is to form the carbonyl of the thioxanthone is present in the disulphide chosen, and in this case the starting material may be di-*o*-thiobenzoic acid or its derivatives, which are submitted to condensation with any aromatic compound.

(2) In the second type the carboxyl is present in the aromatic compound chosen for condensation. Here any suitable disulphide may be chosen for condensation with suitably substituted derivatives of benzoic acid; for example, *m*-hydroxybenzoic acid.

It is obvious that either of these methods may be varied to a very great extent; but since no useful end would be served in preparing numerous complex derivatives of thioxanthone, we have limited our experiments to mere illustration.

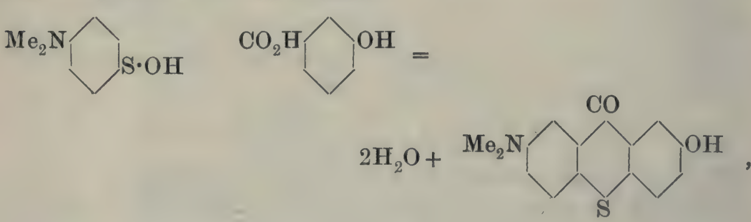
To exemplify the first type of synthesis, di-*o*-thiobenzoic acid has been condensed chiefly with disubstituted derivatives of benzene of varying character: halogen derivatives, phenol, and hydrocarbons. The thioxanthones which are formed contain one of the aromatic nuclei unsubstituted; for example:



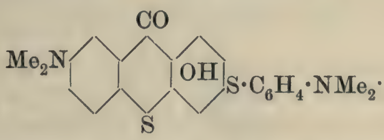
To illustrate the second type of synthesis, *p*-dithiodimethylaniline has been condensed with *m*-hydroxybenzoic acid. It has been shown that on the condensation of this disulphide with phenol, the greater portion of the product consists of complex substances, which are formed by the further action of the sulphoxylic acid,

$$Me_2N \cdot C_6H_4 \cdot SOH,$$

on the initial unsymmetrical sulphide. A similar type of reaction has been observed with *m*-hydroxybenzoic acid; for the product is not the simple hydroxydimethylaminothioxanthone which might be expected according to the scheme:

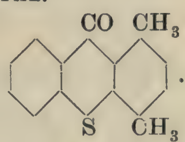


but is the dimethylaminophenylthiol derivative of this:



Two isomeric substances have been isolated from this process; they probably differ in the varying situation of the $\cdot S \cdot C_6H_4 \cdot NMe_2$ residue.

Experimental.

1 : 4-*Dimethylthioxanthone*, 

The di-*o*-thiobenzoic acid employed in these experiments was obtained by oxidising *o*-thiolbenzoic acid with ferric chloride (Prescott and Smiles, this vol., p. 644). This acid, in quantities of about 10 grams at a time, was mixed with 50 c.c. of concentrated sulphuric acid and excess of *p*-xylene. Interaction immediately began with evolution of sulphurous acid, but it was hastened to completion by warming the mixture on the water-bath to 50° for three-quarters of an hour. During the process the mixture was constantly shaken. The precipitate, which separated on pouring the mixture into water, was collected, and washed with water; finally, it was treated with aqueous alkali hydroxide to remove any unchanged dithio-acid. The solid residue was again collected, and washed with water until free from alkali hydroxide. Recrystallisation of the dried substance from boiling alcohol furnished 1 : 4-*dimethylthioxanthone* in short, yellow needles, which melted at 112°:

0·1910 gave 0·5234 CO_2 and 0·0866 H_2O. C=74·7; H=5·0.

$C_{15}H_{12}OS$ requires C=75·0; H=5·0 per cent.

The substance exhibits a bright fluorescence in most organic solvents; the solution in concentrated sulphuric acid shows a yellow fluorescence. In the preparation of this substance it is important to observe that the acid solution should not be heated much above the limit given; otherwise, very insoluble products—probably bisthioxanthones—are formed.

1:3-*Dimethylthioxanthone*, $C_6H_4<{CO \atop S}>C_6H_2Me_2$.

The condensation of di-*o*-thiobenzoic acid was conducted with *m*-xylene, as just described with *p*-xylene. The product crystallised from boiling alcohol in silky, yellow needles, which melted at 127°. The substance exhibits a blue fluorescence in alcoholic solution, and a green in sulphuric acid:

0·1860 gave 0·5100 CO_2 and 0·0870 H_2O. C=74·7; H=5·2.
$C_{15}H_{12}OS$ requires C=75·0; H=5·0 per cent.

Bromothioxanthone, $C_6H_4<{CO \atop S}>C_6H_3Br$.

The condensation of bromobenzene and di-*o*-thiobenzoic acid was carried out as before. The product was crystallised from alcohol, when it was obtained in minute, yellow needles, which melted at 141°:

0·1930 gave 0·3790 CO_2 and 0·0408 H_2O. C=53·5; H=2·3.
$C_{13}H_7OBrS$ requires C=53·6; H=2·4 per cent.

Chloroethoxythioxanthone, $C_6H_4<{CO \atop S}>C_6H_2Cl\cdot OEt$.

p-Chlorophenetole was condensed with di-*o*-thiobenzoic acid by means of warm sulphuric acid. The product was freed from acid impurities by means of alkali, and then recrystallised from boiling alcohol; *chloroethoxythioxanthone* was thus obtained in slender, yellow needles, which melted at 144°:

0·1986 gave 0·4528 CO_2 and 0·0748 H_2O. C=62·6; H=4·1.
$C_{15}H_{11}O_2ClS$ requires C=62·7; H=3·8 per cent.

Chlorohydroxythioxanthone, $C_6H_4<{CO \atop S}>C_6H_2Cl\cdot OH$.

A mixture of di-*o*-thiobenzoic acid and excess of *p*-chlorophenol was warmed on the water-bath with concentrated sulphuric acid. When the interaction was complete, the mixture was poured into water, and the solid precipitate was collected and redissolved in aqueous alkali hydroxide. The phenol was liberated from this solution by saturation with carbon dioxide; it was collected and recrystallised from alcohol, in which it is sparingly soluble. Finally, the chlorohydroxythioxanthone was obtained in yellow needles, which melted at 253°:

0·2010 gave 0·1094 AgCl. C = 13·5.

0·1076 „ 0·2362 CO_2 and 0·0305 H_2O. C = 59·8; H = 3·1.

$C_{13}H_7O_2ClS$ requires C = 59·4; H = 2·6; Cl = 13·5 per cent.

The *sodium* salt of this phenol forms orange needles, which are sparingly soluble in cold water. The substance exhibits a faint green fluorescence in sulphuric acid, the solution being orange.

Condensation of Di-p-thiodimethylaniline.

Preliminary experiments on the condensation of this disulphide with *m*-hydroxybenzoic acid showed that in sulphuric acid the second molecular proportion of the dimethylanilinesulphoxylic acid, $NMe_2 \cdot C_6H_4 \cdot S \cdot OH$, united with the thioxanthone which was produced by condensation of the first with the *m*-hydroxybenzoic acid (see p. 643). Therefore, in order to obtain maximum yields of the product, the disulphide and *m*-hydroxybenzoic acid were employed in equimolecular proportions. The solution of these substances in concentrated sulphuric acid was heated at 60—70° on the water-bath until evolution of sulphurous acid had ceased. This usually occupied about an hour, and after the lapse of that time the solution had become dark red. The mixture was then poured on crushed ice, and the liquid was rendered alkaline with sodium carbonate. After the mixture had been kept for some hours, the precipitated material solidified; this was collected, and as completely as possible freed from excess of alkali by washing with water. On treating the product with hot alcohol, a considerable portion readily dissolved, whilst the residue was almost insoluble. The latter was recrystallised from boiling phenetole, in which it was sparingly soluble. The *dimethylaminophenylthiol* derivative of *hydroxydimethylaminothioxanthone* which was thus obtained formed garnet-coloured prisms. When rapidly heated, the substance melts at 250°; it is sparingly soluble in most organic media, and the dilute solution in chloroform exhibits a green fluorescence:

0·1075 gave 0·2564 CO_2 and 0·0514 H_2O. C = 65·0; H = 5·3.

0·1515 „ 0·1698 $BaSO_4$. S = 15·4.

$C_{23}H_{22}O_2N_2S_2$ requires C = 65·4; H = 5·2; S = 15·1 per cent.

The salts of this base are sparingly soluble, yellow substances; the *platinichloride* was obtained by adding chloroplatinic acid to an alcoholic solution of the chloride. It forms an insoluble yellow powder of high melting point. Attempts to purify the substance were not successful on account of its insolubility in common media and instability in solvents of high boiling point. A sample which had been dried at 100° was analysed:

0·1478 gave 0·0328 Pt. Pt = 22·2.

$C_{23}H_{22}O_2N_2S_2,H_2PtCl_6$ requires Pt = 22·9 per cent.

The scarlet sodium salt of this thioxanthone derivative is insoluble in cold water, and is decomposed by carbonic acid.

That portion of the original product which was soluble in hot alcohol was reprecipitated by the addition of water and a little glacial acetic acid. This process was repeated several times until a substance of constant composition was obtained. The product formed a bright orange powder of similar properties to the thioxanthone derivative previously described. It is more soluble in organic media than that substance, and exhibits a brighter fluorescence in chloroform solution; the sodium salt and hydrochloride also are more soluble in water. Analysis showed that the substance is undoubtedly an isomeride containing an additional molecular proportion of water. The data quoted were obtained with samples from different preparations dried in a vacuous desiccator:

0·1074 gave 0·2456 CO_2 and 0·0350 H_2O. C = 62·36; H = 5·7.
0·1123 „ 0·2563 CO_2 „ 0·0580 H_2O. C = 62·2; H = 5·2.
0·1650 „ 8·2 c.c. N_2 (moist) at 14° and 76 mm. N = 5·9.
$C_{23}H_{22}O_2N_2S_2,H_2O$ requires C = 62·7; H = 5·4; N = 6·3 per cent.

When heated in the steam-oven the substance contracts with partial loss of water, but this could not be estimated for; even at 150° it is not completely expelled, and the substance then begins to decompose.

The yield of these two derivatives of thioxanthone was almost theoretical.

In conclusion, we desire to thank the Research Fund Committee of the Society for a grant which has defrayed the expenses of these experiments.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE, LONDON.

CLIII.—*The Dissociation Pressures of Alkali Bicarbonates. Part I. Sodium Hydrogen Carbonate.*

By Robert Martin Caven and Henry Julius Salomon Sand.

It is the object of the present investigation to study the dissociation pressures of the various alkali bicarbonates in order to discover to what extent the relative stability of each is connected with the basigenic behaviour of its metal, and the position of the latter in the periodic system. The equilibria which must be investigated for this purpose may be expressed by the equation:

$$2MHCO_3 \rightleftharpoons M_2CO_3 + H_2O + CO_2,$$

in which M indicates the atom of an alkali metal. This equation represents in its most general form a three-component equilibrium, but, as will be seen in the sequel, it is sufficient for the purpose we have in view to treat it as one derived from the two components $MHCO_3$ and M_2CO_3, whereby we limit ourselves to the case in which water and carbon dioxide occur in equimolecular proportions in the gaseous phase.

Exact data connected with the subject are very scarce. In 1835 Rose (*Pogg. Ann.*, 1835, **34**, 158) proved that solutions of sodium and potassium hydrogen carbonates may decompose at the ordinary temperature, yielding the normal carbonate and carbon dioxide, and the same conclusion has been arrived at in different ways by several other experimenters (Magnus, *Pogg. Ann.*, 1837, **40**, 590; Marchand, *J. pr. Chem.*, 1845, **35**, 389; Treadwell and Reuter, *Zeitsch. anorg. Chem.*, 1898, **17**, 202).

Corresponding results for solid sodium hydrogen carbonate were obtained by Gautier in 1876, when temperatures above 35° were employed (*Ber.*, 1876, **9**, 1434). In connexion with his work on the solubilities of alkali bicarbonates, Dibbits, in 1874, determined approximately the partial pressure of carbon dioxide which was in equilibrium with saturated solutions of the respective salts at various temperatures (*J. pr. Chem.*, 1874, [ii], **10**, 440). Lescoeur, in 1892, attempted to measure the dissociation pressure of solid sodium hydrogen carbonate between 55° and 100°, but does not appear to have obtained a true equilibrium, since the recorded results are very much lower than ours (*Ann. Chim. Phys.*, 1893, [vi], **28**, 423). Lastly, McCoy, in 1903, carefully studied the equilibrium at 25° between a solution containing sodium carbonate and sodium hydrogen carbonate and a gaseous phase composed of air, carbon dioxide, and water vapour (*Amer. Chem. J.*, 1903, **29**, 437).

Experimental.

Method and Apparatus.—The experiments which we have carried out consist in determining the vapour pressures produced on heating a mixture of sodium hydrogen carbonate and anhydrous sodium carbonate. It is not a priori clear whether only the phases, anhydrous sodium carbonate, sodium hydrogen carbonate, and vapour, will be thus produced, or whether sodium carbonate monohydrate will also be formed, so that the four phases, anhydrous sodium carbonate, sodium carbonate monohydrate, sodium hydrogen carbonate, and vapour, corresponding with a three-component equilibrium, will be present.

If the former is the case, the partial pressure of the water vapour in the gaseous phase will be smaller than the vapour pressure of sodium carbonate monohydrate; and the combined pressures of carbon dioxide and water, which are equal, will be less than twice as great as the dissociation pressure of the monohydrate.

If the latter is the case the partial pressure of the water vapour will be equal to the vapour pressure of sodium carbonate monohydrate, and the partial pressure of the carbon dioxide greater than that of the water vapour, because some water will have been removed from the gaseous phase to form the monohydrate.

The total observed pressure due to carbon dioxide and water vapour will thus be more than twice as great as the vapour pressure of sodium carbonate monohydrate.

A comparison of the vapour pressure of sodium carbonate monohydrate with that of sodium hydrogen carbonate will therefore render a decision between the two alternatives possible; and actual measurements have proved that sodium carbonate monohydrate does not exist in the equilibrium mixture under the conditions of our experiments.

The method of working consisted in heating the mixture of sodium carbonate and sodium hydrogen carbonate in an evacuated flask contained in a thermostat. The vapour generated was accurately balanced against some air, the pressure of which was adjustable, a small gauge consisting of a U-tube containing mercury, which was sealed to the flask, and was also contained in the thermostat, serving as the zero instrument.* The pressure was then read on a manometer.

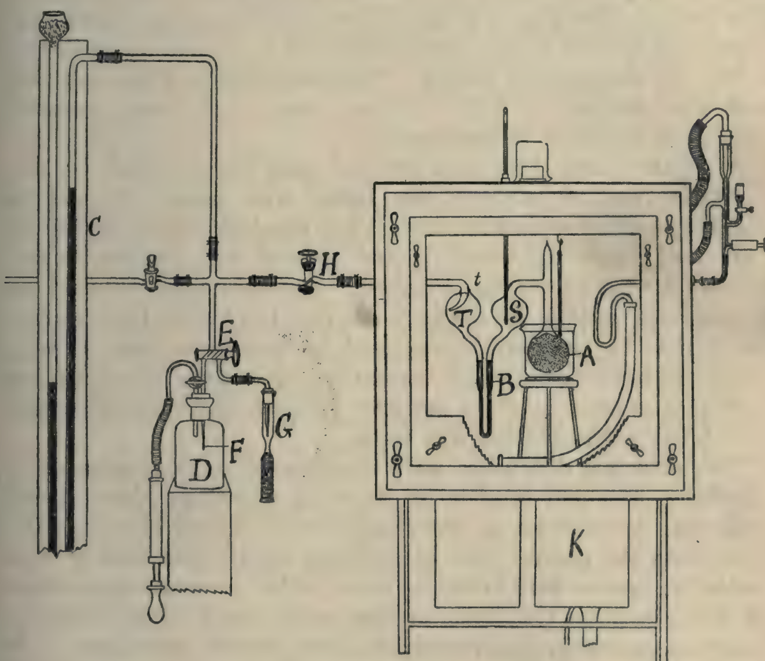
The apparatus was arranged so that it could be laid on its side

* Since these experiments were begun a very similar method for the measurement of vapour pressures has been described by Johnston (*Zeitsch. physikal. Chem.*, 1908, 62, 333).

without disconnecting during evacuation. Two special bulbs were provided for holding the mercury during this operation.

Fig. 1 shows the apparatus. *A* is the flask containing the reaction mixture, *B* the small mercury gauge, and *C* the manometer. *S* and *T* are the two bulbs just referred to. It will be seen that *T* is fitted with a trap *t*, which makes it possible to withdraw gas from the flask through the mercury without risk of allowing the latter to splash into the exit tubes of the apparatus. The bottle *D* can be either evacuated or fitted with compressed air, according as the

FIG. 1.



pressure to be read is smaller or greater than that of the atmosphere. According to the position of the three-way tap *E*, air can be cut off, or either allowed to enter or leave the apparatus very slowly through the capillaries *F* and *G*, thus permitting the levels of the mercury in the gauge *B* to be very accurately adjusted. The tap *H* was added for further convenience in manipulation.

The general construction of the air thermostat will be clear from the figure. As will be seen, it is double-walled, the products of combustion of the gas from the burner passing up the chimney *K* and between the two walls. Each jacket is provided with a remov-

able transparent front. The apparatus is made of sheet iron, and heavily coated with asbestos outside. Wide steel tubes passing through both jackets are fitted where openings are necessary. The regulator is of the Ostwald pattern, and is filled throughout with mercury. The tubes inside the thermostat are of steel, and are attached to those outside, which belong to a glass regulator of a commercial type, by means of a short, thick-walled rubber connexion.

All the steel joints are screwed, and made mercury-tight by means of oil and red lead. It was found that excellent constancy of temperature was obtained by immersing the flask of the tensimeter in a beaker containing slightly diluted sulphuric acid. Mechanical stirring of the air of the thermostat was tried, but discarded, as it did not improve the results. The temperature of the sulphuric acid was constant to 0·2°. It was read on a small, carefully calibrated Anschütz thermometer.

After the gauge had been charged with mercury and the flask with the reaction mixture, the latter was sealed off, and the necessary rubber connexion made. Thick-walled rubber tubing was employed, which was wired on and covered with shellac varnish; thus an air-tight joint was obtained. The tensimeter was then laid horizontally, so that the mercury ran into the bulbs; the apparatus could then be completely evacuated by employing first a water-pump, and then a Sprengel mercury-pump. After the tensimeter had been turned into the upright position, and the thermostat closed, the determination was begun.

Two principal difficulties were encountered in the course of the research. The first consists in obtaining a gaseous phase of equimolecular proportions of water-vapour and carbon dioxide. It is clear from the general laws of chemical equilibrium that if either molecular species were in excess, owing either to selective absorption of the other by the walls of the vessel, or to the presence of adsorbed water in the reaction-mixture or the apparatus, a too high result would be obtained for the decomposition pressure. The second difficulty was due to retardation in the establishment of equilibrium, and was doubtless the result of impermeable crusts formed on the reaction mixture.

We tried to meet the first difficulty by very carefully drying the apparatus before use, gently igniting the sodium carbonate, and leaving the sodium hydrogen carbonate in a desiccator over sulphuric acid for a considerable time before mixing it with the sodium carbonate. A transparent silica vessel was also tried. It was finally found necessary, however, to withdraw large quantities of gas evolved from the reaction mixture at high temperature, and

to continue the process of withdrawal until the readings obtained after two successive withdrawals were identical. The use of the silica vessel was abandoned in the later experiments.

The second difficulty gave a very great deal of trouble, and may very probably be the cause that the results here recorded have been hitherto unknown.

In order to obtain satisfactory readings, it was found necessary to take an amount of sodium hydrogen carbonate which was approximately five hundred-fold that theoretically required to evolve the necessary volume of gas at the highest pressure reached in the experiments. The excess of carbonate sufficient for the re-absorption of the gases on cooling was much smaller than this, an approximately fifty-fold value being sufficient. It is clear that retardation, owing to the formation of crusts, will cause the results to be too low when the temperature is being raised, and too high when it is being lowered. The results will be correct when the same value is obtained in both cases. It was thus found that only from 95° onwards could correct values be obtained on raising the temperature; and in the case of the lowest of these about ten days were necessary for the complete establishment of equilibrium.

On lowering the temperature constant readings were obtained much more rapidly. There is little doubt, moreover, that the numbers obtained in the latter case are substantially correct to about 85°, since they lie on the curve extrapolated from readings taken at higher temperatures.

The rate at which the reaction-mixture was heated was also found to have an effect, rapid heating tending to prevent retardation; the retardation was greatest after all trace of excess of water had been removed as described above.

Sodium Carbonate Monohydrate.

Table I gives the results obtained for the vapour pressure of sodium carbonate monohydrate. This salt was prepared by heating sodium carbonate decahydrate in a shallow dish on the water-bath until the mass had just become solid again after fusion. The product, after thorough mixing, contained 14·3 per cent. of water, instead of 14·45 according to theory.

A mixture of 40 grams of this salt with 4 grams of the anhydrous carbonate was employed in the experiment.

TABLE I.

Temp. rising. Temp.	Pressure mm. Hg. Observed.	Calculated.	*Temp. falling.* Temp.	Pressure mm. Hg. Observed.	Calculated.
30·5°	7·9	8·7	92·7°	419·9	418·0
40·4	15·9	17·9	86·4	297·1	301·0
51·0	36·6	36·9	80·3	216·1	216·0
57·1	53·6	54·6	70·1	121·7	121·0
66·4	93·2	96·8	60·5	69·4	67·5
76·4	166·6	173·0	50·2	39·2	34·9
83·1	243·4	251·0	41·1	23·0	18·8
90·3	363·4	369·0	30·9	13·1	9·0
97·7	539·1	540·0	17·5	6·7	3·1

As is well known, the results of vapour-pressure experiments may be expressed with a considerable degree of accuracy by a formula of the type:

$$\log p = a - \frac{b}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

in which p is the vapour pressure, T the absolute temperature, and a and b are constants; b is connected with the heat of reaction q per gram-molecule of gas produced, by the formula:

$$q = \log_e 10 R b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

in which the gas constant R equals 2 calories per gram-molecule per degree, and $\log_e 10 = 2{\cdot}30$.

In the third column of table I values of p are calculated from equation (1) by making $a = 10{\cdot}825$; $b = 3000{\cdot}0$. It will be seen that the majority of the observed values agree closely with the calculated ones, the numbers obtained on raising the temperature being generally very slightly lower, and those found on lowering it, very slightly higher than the calculated values. The curve for sodium carbonate monohydrate is shown in Fig. 2.

Sodium Hydrogen Carbonate.

Table II contains a complete series of determinations of the decomposition pressure of sodium hydrogen carbonate.

A mixture of 50 grams of sodium hydrogen carbonate and 5 grams of sodium carbonate was taken, the constituents being dried separately in the manner described above, and then mixed. The same mixture was heated and cooled repeatedly for the purpose of obtaining the numbers given, as will be clear from the table.

The approximate quantities of gas withdrawn at various times and temperatures are shown. As will be readily understood, a knowledge of these quantities could be gained by a simple calculation, after withdrawing the gas into the bottle D (Fig. 1), of known

capacity (600 c.c.), and noting the pressure in the latter before and afterwards. It should be mentioned here that the fact that no air leaked in while gas was being withdrawn past the mercury has been proved repeatedly by cooling the apparatus to atmospheric temperature, and noticing that the pressure ultimately fell practically to zero.

The calculated values have been derived from equation (1) after making $a = 11{\cdot}8185$ and $b = 3340$. It will be seen that at high temperatures the agreement is fairly close throughout, the experimental numbers obtained on lowering the temperature being usually slightly higher, and those found on raising it slightly lower than the calculated values. Those numbers which have obviously been considerably vitiated by "retardation" are enclosed in brackets.

Table III gives the results of some earlier experiments, which will be found in the main to confirm those of table II. The

TABLE II.

		Pressure in mm. of mercury.			
		Observed.			
Series.	Temp.	Rising.	Falling.	Calculated.	Approx. vol. of gas withdrawn.
(I.)	90·0°	—	—	—	38 c.c.
	92·4	467·5	—	476·0	—
	104·1	—	936·6	915·0	—
	97·1	—	633·5	625·5	—
	89·6	—	(426·5)	405·0	—
	43·7	—	(51·2)	19·0	—
(II,)	107·0	—	—	—	38 c.c.
	108·4	1153·5	—	1151·4	—
	101·9	—	821·9	811·3	—
	92·0	—	473·3	465·1	—
	75·2	—	(210·5)	168·3	—
	49·9	—	(70·6)	29·7	—
(III.)	105·0	—	—	—	56 c.c.
	114·4	1594·8	—	1574·0	—
	112·4	—	1413·5	1420·0	—
	107·8	—	1106·7	1116·0	—
	101·2	—	776·2	781·0	—
	93·3	—	507·3	502·0	—
	84·1	—	308·8	292·0	—
	41·5	—	(30·1)	16·0	—
(IV.)	88·2	(153·9)	—	499·0	—
	95·8	567·7	—	578·0	—
	95·8	—	—	—	49 c.c.
	95·8	563·4	—	578·0	—
	102·8	836·5	—	853·0	—
	101·4	—	790·8	790·0	—
	101·4	—	—	—	31 c.c.
	101·8	808·6	—	807·5	—
	106·4	1033·2	—	1035·4	—
	107·4	1102·1	—	1093·0	—
	106·6	—	1043·6	1046·7	—

TABLE III.

Series.	Temp.	Pressure in mm. of mercury. Observed. Rising.	Falling.	Calculated.	Approx. vol. of gas withdrawn.
(I.)	107·4°	1097·6	—	1092·2	—
	111·7	1391·7	—	1369·0	—
	111·7	—	—	—	Large unknown vol.
	115·1	1662·9	—	1631·0	—
	111·9	—	1391·7	1383·0	—
	107·7	—	1111·9	1109·0	—
	102·6	—	847·1	843·0	—
	98·7	—	691·7	680·0	—
	92·1	—	485·6	468·0	—
	85·5	—	(350·7)	317·5	—
	7·5	—	(2·3)	0·8	—
(II.)	110·9	1422·1	—	1313·3	—
	110·9	—	—	—	271 c.c.
	114·3	1642·2	—	1565·7	—
	106·9	1118·6	—	1063·5	—
	106·9	—	—	—	51 c.c.
	107·6	1130·8	—	1103·8	—
	107·6	—	—	—	39 c.c.
	107·6	1098·0	—	1103·8	—
	107·6	—	—	—	35 c.c.
	107·3	—	1091·0	1086·0	—
	105·0	—	978·5	960·0	—
	111·7	1399·2	—	1369·0	—
	115·5	1646·9	—	1664·2	—
	111·2	—	1325·7	1333·5	—
	108·4	—	1155·9	1151·0	—
	104·3	—	937·4	925·0	—
	99·4	—	743·0	707·0	—
	93·6	—	(570·1)	510·0	—
	19·4	—	(11·2)	2·5	—

amounts of substance taken for the determinations were 40 and 4 grams of sodium hydrogen carbonate and sodium carbonate respectively in series (i), and 50 and 5 grams respectively in series (ii).

The dissociation pressure curve of sodium hydrogen carbonate is shown in Fig. 2, together with that of sodium carbonate monohydrate. The curves themselves correspond with the equations, the observed values being indicated in the following manner:

⊙ = temp. rising; × = temp. falling.

It can be shown readily that if the equations derived from our experiments hold for the vapour pressures of sodium carbonate monohydrate and sodium hydrogen carbonate respectively, then the values of the former will be more than half as great as those of the latter at all temperatures below 218°; and that there is thus no possibility of the four-phase equilibrium: anhydrous sodium carbonate, sodium carbonate monohydrate, sodium hydrogen

carbonate, vapour, having been produced in our experiments (see p. 1360).

The vapour pressure corresponding with this four-phase equilibrium may now be calculated. Indicating this pressure at any temperature by p, the corresponding partial pressures of the water vapour and carbon dioxide by p' and p'' respectively, we have:

$$p = p' + p''.$$

The quantity p' is the same as the dissociation pressure of sodium carbonate monohydrate, and may be obtained from the equation we have given for the latter.

The values of p'' may be derived as follows:

If we indicate the dissociation pressure of sodium hydrogen carbonate as obtained by the equation derived for it above by p_1, then the partial pressure of the water vapour and of the carbon dioxide may each be taken as $p_1/2$, and by applying the law of mass action we find:

$$p'' = \frac{\left(\frac{p_1}{2}\right)^2}{p'} .$$

In this way the values given in table IV have been arrived at. The corresponding numbers for the three-phase equilibrium at the same temperature, which are always a little lower, are given for comparison. The curve for the four-phase equilibrium is also shown in Fig. 2. An attempt was made to verify these numbers experimentally with a mixture of 20 grams of sodium hydrogen carbonate, 15 grams of sodium carbonate monohydrate, and 10 grams of anhydrous sodium carbonate; but the retardation in the pressure values was so great that the experiment was abandoned.

TABLE IV.

Pressure in mm. of Mercury.

	Four-phase equilibrium.			
Temp.	H_2O.	CO_2.	Total.	Three-phase equilibrium.
30°	8·4	1·2	9·6	6·2
50	34·4	6·5	40·9	30·0
70	119·9	30·2	150·1	120·4
90	364·0	117·8	481·8	414·3
100	605·4	220·8	826·2	731·1
110	981·8	399·0	1380·8	1252·6

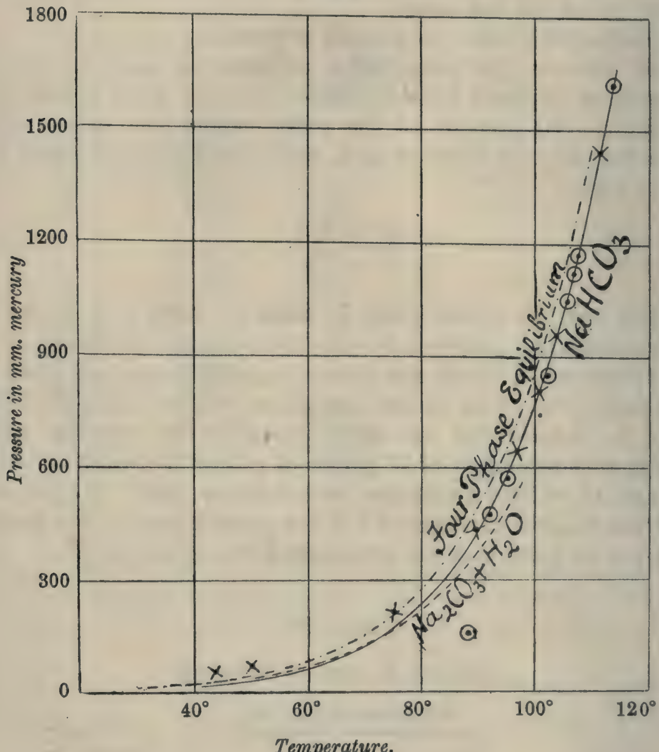
Heats of Dissociation.—By applying equation 2, the heats of dissociation per gram-molecule of gas produced are calculated to be: for sodium carbonate monohydrate, 13,800 calories, and for sodium hydrogen carbonate, 15,360 calories.

Therefore, employing Planck's notation, we have:

$$[Na_2CO_3,H_2O]=[Na_2CO_3]+\{H_2O\}-13,800.$$
$$2[NaHCO_3]=[Na_2CO_3]+\{H_2O\}+\{CO_2\}-30,700.$$

It is interesting to compare the last-named heat-toning with a value for the same reaction derived from direct thermochemical measurements. According to de Forcrand (*Compt. rend.*, 1909, **149**, 719), the heats of formation from their elements of 1 gram-

FIG. 2.



molecule of sodium hydrogen carbonate and carbonate are respectively 228,380 and 271,970 calories. Taking the corresponding value for water (as steam at 100°) as 58,060 calories, and for carbon dioxide as 97,000 calories, we have, in Planck's notation:

$$[NaHCO_3]=-228,380,\ [Na_2CO_3]=-271,970,$$
$$\{H_2O\}=-58,060,\ \{CO_2\}=-97,000,$$

and substituting these values in the equation

$$2[NaHCO_3]=[Na_2CO_3]+\{H_2O\}+\{CO_2\}-x,$$

we find $x = 29{,}700$ calories, instead of 30,700 calories, the figure derived from our experiments.

In view of the indirect nature of the method of comparison, this agreement must be considered quite satisfactory.

Summary.

The vapour pressure in mm. of mercury of sodium carbonate monohydrate can be represented with sufficient accuracy by the equation:

$$\log p = 10{\cdot}825 - \frac{3000{\cdot}0}{T},$$

that of sodium hydrogen carbonate by the equation:

$$\log p = 11{\cdot}8185 - \frac{3340}{T}.$$

From the former equation the heat of dissociation of one gram-molecule of sodium carbonate monohydrate is calculated to be 13,800 calories; from the latter, that of two gram-molecules of sodium hydrogen carbonate to be 30,700 calories.

The pressure-values corresponding with the four-phase equilibrium, anhydrous sodium carbonate, sodium carbonate monohydrate, sodium hydrogen carbonate, vapour, have been calculated. They are somewhat higher than the vapour pressure of sodium hydrogen carbonate at all temperatures falling within the range of our experiments.

We take this opportunity of expressing our indebtedness to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

University College,
Nottingham.

CLIV.—*The Relation of the Velocity of Chlorination of Aromatic Compounds to Constitution. Part I. Chlorination of Anilides.*

By Kennedy Joseph Previté Orton and Harold King.

Although it is well known that differences exist in the "readiness" with which anilides are chlorinated or brominated, no systematic study of the relation between the velocities of substitution and constitution has been made.

The investigation is beset with numerous difficulties. The forma-

tion of the compound of hydrogen bromide and bromine: $HBr + Br_2 \rightleftarrows HBr_3$, especially in anhydrous solvents, obscures the process of bromination (*Brit. Assoc. Reports*, 1910, p. 85; Orton and Jones, Proc., 1909, **25**, 305; Jones, this vol., 392). The similar compound of chlorine and hydrogen chloride, if produced at all under analogous conditions, is at such low concentrations as to have no detectable effect on chlorination. Hence we have, in the first place, confined our attention to chlorination.

The process of chlorination is very greatly affected by the medium in which it takes place. For reasons which will appear in what follows, a true comparison of the speeds of chlorination can best be made in glacial acetic acid. Orton and Jones (Trans., 1909, **95**, 1456) have shown that in acetic acid of various dilutions there exists an equilibrium between chlorine, anilide, chloroamine, and hydrogen chloride: $Ar{\cdot}NH{\cdot}Ac + Cl_2 \rightleftarrows Ar{\cdot}NCl{\cdot}Ac + HCl$. In glacial acetic acid the right hand side of the system cannot be detected, but as the medium is diluted, it becomes perceptible; for example, in 95 per cent. acetic acid it forms 20 per cent. of the system; in 75 per cent. acetic acid, 80 per cent.; and finally, in 50 per cent. acetic acid, only a trace of free chlorine is present. These numbers refer to 2:4-dichloroacetanilide, but although in dilute acetic acids there is considerable difference between anilides, in glacial acetic acid the constitution of the anilide has little effect. This equilibrium is attained with extreme rapidity, but in one or two selected instances the velocity of the opposing reactions has been indirectly measured (*Brit. Assoc. Reports*, *loc. cit.*).

This reversible formation of chloroamine complicates greatly the process of chlorination in the nucleus, *C*-chlorination, in dilute acetic acid. When chlorine is added to an aqueous acetic solution of an anilide which is capable of *C*-chlorination, such as *p*-chloroacetanilide, two reactions, both extremely fast, take place, irreversible *C*-chlorination and reversible *N*-chlorination:

$$Ar{\cdot}NH{\cdot}Ac + Cl_2 \begin{array}{l} \rightleftarrows Ar{\cdot}NCl{\cdot}Ac + HCl \\ \searrow ArCl{\cdot}NH{\cdot}Ac + HCl \end{array} .$$

The proportion of the two changes, and hence their relative velocities, can be very easily measured by estimations of the free chlorine (by aspiration) and of the chloroamine (by titration) (Orton and Jones, *loc. cit.*). It varies with the composition of the medium and the constitution of the anilide: thus for *p*-chloroacetanilide, the ratio, *N*-chlorination/*C*-chlorination, in 30 per cent. acetic acid, is 0·93:1; in 50 per cent., 1·25:1; in 65 per cent., 1·55:1, whilst for acetanilide, in the same concentrations of acetic acid, 0·082:1, 0·08:1, and 0·083:1.

The absence of *N*-chlorination, and the fact that *C*-chlorination is slowest in glacial acetic acid, allows of direct measurement of the speeds of *C*-chlorination, and a comparison of different anilides in this medium, which has therefore been chosen for a study of the effect of constitution of anilides.

In selecting a method of experiment, it must be remembered, as shown in the foregoing, that the same velocity of chlorination is found when the reacting system is prepared from chlorine and anilide, or chloroamine and hydrochloric acid, since chloroamines and hydrogen chloride in glacial acetic acid react quantitatively and instantly, forming chlorine and anilide. For a similar reason, as a very convenient way of adding given quantities of chlorine, an anilide, the speed of chlorination of which is under investigation, may be treated with the molecular proportions of hydrogen chloride and some chloroamine, such as acetylchloroamino-2:4-dichlorobenzene, the anilide corresponding with which is not chlorinated in the nucleus at an appreciable rate. This last procedure is in every way to be perferred, for the preparation of standard solutions of chlorine in glacial acetic acid, or the preparation of chloroamines often difficult to purify, is avoided. Moreover, the simplification of the manipulation lessens the opportunity for the introduction of small quantities of water, which has a powerful accelerating effect on the velocity of chlorination. We have put these three methods of operating to a thorough experimental test, and have shown that the value of the velocity coefficient is independent of the procedure, and, further, of the order in which the three reagents are mixed.

The speed of chlorination in glacial acetic acid is independent of the quantity of hydrogen chloride, provided that the acid is in excess of one molecular proportion. When a chloroamine is used as chlorinating agent, and but a relatively small proportion of hydrogen chloride, 1/20—1/10th gram-molecular proportion, added, the concentration of the chlorine in the system remains constant at 1/20—1/10th gram-molecular proportion during the main part of the reaction. Hence the reaction is apparently of the first order. Moreover, since the quantity of chlorine produced in the system is equivalent to the hydrogen chloride added, the speed of chlorination is proportional to the concentration of the acid. When the chlorination is carried out by treatment of the isomeric chloroamine with a small proportion of hydrogen chloride (1/20—1/10th gram-mol.), for example, the conversion of acetylchloroamino-*p*-chlorobenzene into 2:4-dichloroacetanilide:

$$ArCl\cdot NCl\cdot Ac[+HCl] \longrightarrow ArCl_2\cdot NH\cdot Ac[+HCl],$$

the speed of chlorination is proportional to the *square* of the concen-

tration of the hydrogen chloride added, for now quantities equivalent to the hydrogen chloride, of both the reacting substances, anilide and chlorine, are produced in the system. These relations only hold in glacial acetic acid, for in the diluted media chloroamine and hydrogen chloride can co-exist.

Experiment has shown that hydrogen chloride may be present in excess to the extent of 8—10 molecular proportions without affecting the character or speed of the chlorination. This behaviour is in marked contrast to the effect of hydrogen bromide on bromination (*loc. cit.*); addition of sufficient excess of hydrogen bromide, 4 gram-molecular proportions, will bring the bromination of acetanilide in glacial acetic acid to a standstill.

The reaction is naturally a simple change of the second order. Whatever view be held as to the mechanism of substitution, the first step is the interaction of separate molecules of anilide and chlorine. There appear to be no disturbing effects produced by change of concentration, or during the course of the reaction. Frequently, of course, a chloroanilide is produced in the reaction, which is itself capable of chlorination. Notwithstanding the fact that its concentration exceeds that of the original anilide for the second half of the reaction, the unchlorinated (or less chlorinated) anilide reacts so much more rapidly (about 200 times) with chlorine than the chlorinated anilide that the effect of the consecutive reaction is scarcely perceptible, even towards the end of the change.

Results: (i) *Acyl Groups.*—The formyl group shows its usual influence; the speed of chlorination reaches a maximum with the propionyl group, but falls off very slightly with increasing length of the acyl chain; the branch chain in *iso*valeranilide has an obvious depressing effect on the velocity.

	k_{II}.		k_{II}.
Formanilide	4·95	Stearanilide	64
Acetanilide	40	*iso*Valeranilide	57
Propionanilide	72	Oxanilide	2
Butyranilide	64·5	Benzanilide	42

(ii) The effect of the presence of chlorine in the ortho- or para-positions respectively is well shown by the following numbers:

	k_{II}.		k_{II}.
Acetanilide	40	Benzanilide	42
o-Chloroacetanilide	0·073	*p*-Chlorobenzanilide	0·16
p-Chloroacetanilide	0·21		

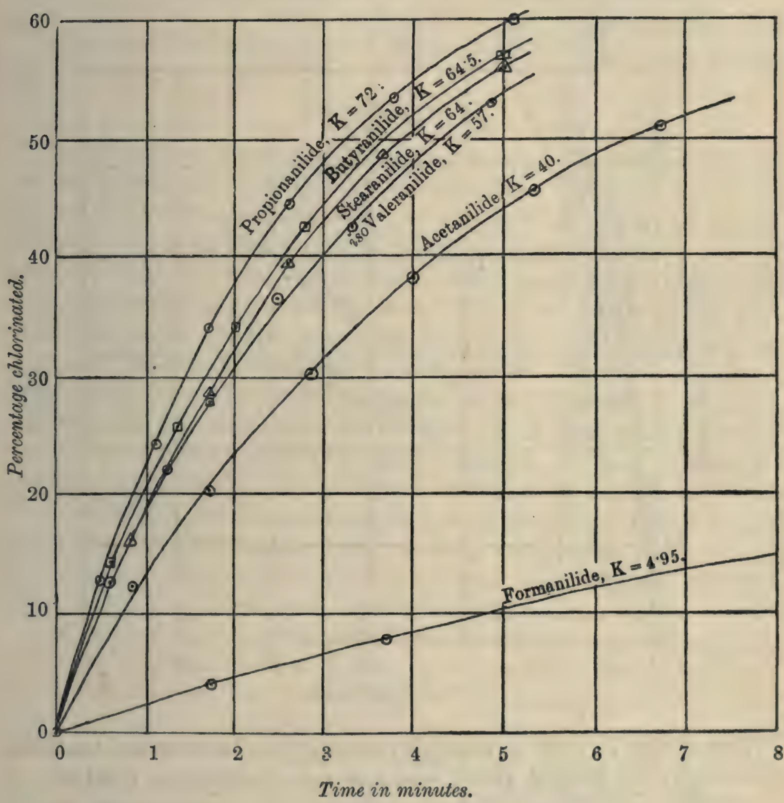
The striking effect of the chlorine atom in the ortho-position is noteworthy. The chlorination of 2:4-dichloroacetanilide in glacial acetic acid cannot be detected at the ordinary temperature; *s*-trichloroacetanilide is produced at 150—160°, but the yield is

poor, as the attack of chlorine on the acetic acid solvent is then considerable.

(iii) Chlorine offers a marked contrast to the methyl group:

	k_{II}.		k_{II}
Acetanilide	40	Benzanilide	42
Aceto-*o*-toluidide	9	Benzo-*o*-toluidide	5·7
Aceto-*p*-toluidide	77	Benzo-*p*-toluidide	70
p-Chloroacetanilide	0·21	*p*-Chlorobenzanilide	0·16

FIG. 1.



The methyl group in the para-position causes an increase in the speed of chlorination; but the influence of position is well shown, in that k_{II} for the chlorination of aceto-*o*-toluidide is only 1/4th that of k_{II} for acetanilide.

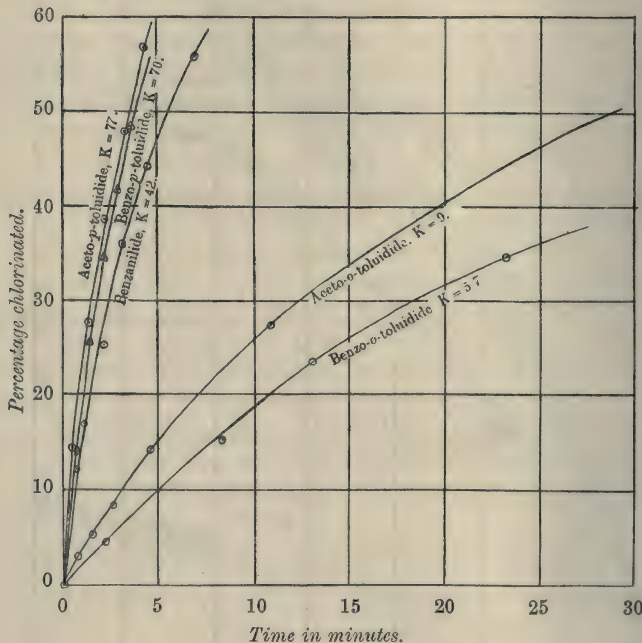
These numbers give also an opportunity of contrasting the acetyl and benzoyl groups. Although benzanilide is chlorinated slightly more rapidly than acetanilide, in the case of the corresponding

derivatives the acetyl compounds are chlorinated about $1\frac{1}{3}$ times as fast as the benzoyl compounds.

(iv) Measurements of the chlorination of anisidides and phenetidides show that the mere occupation of the ortho- or para-positions is not a decisive factor. Aceto-*o*-anisidide and aceto-*o*-phenetidide are chlorinated more rapidly than the para-derivatives.

	k_{II}.		k_{II}.
Acetanilide	40	Aceto-*p*-toluidide	77
Aceto-*o*-anisidide	60	Aceto-*o*-phenetidide	90
Aceto-*p*-anisidide	57	Aceto-*p*-phenetidide	85

FIG. 2.



The ethoxyl group is more favourable to chlorination than the methoxyl; the methyl group occupies an intermediate position.

(v) The cumulative effect of methyl groups is illustrated in the series:

	k_{II}.		k_{II}.
Acetanilide	40	Aceto-*p*-toluidide	77
Aceto-*o*-toluidide	9	Aceto-ψ-cumidide	630
Aceto-*m*-xylidide	9		

The introduction of a methyl group in the para-position with respect to the group NHAc in aceto-*o*-toluidide, as illustrated in aceto-*m*-xylidide, has no effect, whilst the introduction of an ortho-

methyl group in aceto-*p*-toluidide reduces the value of k_{II} to 1/9th 77 to 9. The introduction of a third methyl group, as in ψ-cumidide, is, however, accompanied by a very large rise in the value of k_{II} from 9 to 630.

(vi) The naphthalides are chlorinated at a very high speed.

	k_{II}.		k_{II}.
Acetanilide	40	Formanilide	4·95
Aceto-α-naphthalide	550	Formo-α-naphthalide	365
Aceto-β-naphthalide	"instantaneous chlorination."		

In the case of aceto-β-naphthalide at a concentration of 1/240 gram-molecule per litre, it is impossible to detect free chlorine after mixing.

Experimental.

The procedure which has been found most suitable in making the measurements of the velocity is as follows: A quantity of the anilide (0·00041 gram-molecule) is dissolved in about 15 c.c. of glacial acetic acid, and placed in a stoppered flask. One molecular proportion of acetylchloroamino-2:4-dichloroacetanilide, the source of the chlorine, is dissolved in about 85 c.c. of glacial acetic acid in a 100 c.c. stoppered measuring flask. Both these solutions are allowed to attain the temperature of the bath, 16°. One molecular proportion of hydrogen chloride, in the form of the constant boiling aqueous (22 per cent.) solution (0·058 c.c.), is then added, from a burette graduated to 1/50ths, to the solution of the chloroamine; and then the solution of the anilide immediately introduced. The total volume of the mixture was as nearly as possible 100 c.c., and hence the concentrations of the reacting substances, 0·0041 gram-molecule per litre. The reacting solution was carefully shielded from light in a closed bath kept in a dark room.

Volumes of 10 c.c. were withdrawn by a pipette at appropriate intervals, and added to a 5 per cent. potassium iodide solution; the iodine set free was titrated with $N/50$-thiosulphate.

In the case of anilides with a low solubility in glacial acetic acid, such as oxanilide and stearanilide, the anilide was dissolved in a larger volume of acid, 80—85 c.c., and the chloroamine in the smaller volume (20—15 c.c.). These are mixed, and the hydrogen chloride added finally.

When the speed was low the concentrations were raised to 0·025 gram-molecule per litre.

The anilides were either the purest material supplied by Kahlbaum or prepared from anilines obtained from the same source. They were recrystallised two or three times before use. The *o*-chloroaniline was prepared in the laboratory, and purified by

recrystallising the hydrochloride as described in the following paper (this vol., p. 1381).

Two determinations at least were made of the speed of chlorination, and the anilide was always recrystallised again before the second measurement. The values given for k_{II} in the foregoing are the mean of two concordant experiments.

For the highly dilute solutions which are required for these very speedy reactions, it is essential that the glacial acetic acid should be free from substances which react with chlorine. We used either the special "K" acid supplied by Kahlbaum, or an acid prepared by ourselves by distillation of a good commercial acid from phosphoric oxide. In all cases the acid was shown to be stable to bromine or chlorine (Orton, Edwards, and King, this vol., p. 1178).

Since the speed of chlorination in glacial acetic acid is very sensitive to the addition of water, increasing in a direct ratio, it was very important that the medium should be kept of constant composition throughout the whole series of experiments. We aimed at using an acid melting at 16·3°, that is, it contained 0·14 per cent. of water, as such an acid was far easier to obtain than an absolute acetic acid. Moreover, the addition of a trace of water obviously produces far less effect on the velocity than with an absolute acid. The high or irregular speeds which were occasionally observed could generally be ascribed to accidental entrance of small quantities of water during the manipulations.

The following figures are typical examples of the whole series of experiments. Concentrations are 0·0041, except where otherwise stated:

Formanilide.

Time (minutes).	Percentage chlorinated.	k_{II}.
5·0	8·8	4·75
14·3	21·4	4·75
26·3	33·4	4·75
40·3	43·5	4·77
57·6	53·5	5·00
81·7	62·5	5·10

Acetanilide.

Time (minutes).	Percentage chlorinated.	k_{II}
0·8	12·3	—
1·7	20·3	40
2·8	30·8	40
4·0	38·2	39
5·3	45·6	39
6·7	51·1	39

Propionanilide.

Time (minutes).	Percentage chlorinated.	k_{II}.
0·5	12·9	74
1·1	24·4	73
1·7	34·1	72
2·7	44·5	74
3·8	53·6	74
5·1	60·0	73

Stearanilide.

Time (minutes).	Percentage chlorinated.	k_{II}.
0·8	16·1	63
1·7	28·6	59
2·6	39·5	57
3·7	48·7	57
5·0	56·0	56
6·4	62·4	57

o-*Chloroacetanilide*; conc. 0·025.

Time (minutes).	Percentage chlorinated.	k_{II}.
60·0	10·0	0·074
184·1	24·8	0·072
360·1	40·8	0·076
606·2	53·2	0·075
1007·5	65·3	0·074

p-*Chlorobenzanilide*;

Time (minutes).	Percentage chlorinated.	k_{II}.
69·5	5·6	—
179·2	10·6	0·165
361·4	19·3	0·165
575·2	27·8	0·167
651·0	29·8	0·165
871·2	36·6	0·165

We wish to express our indebtedness to the Government Grant Committee of the Royal Society, and to the British Association, for grants which have partly defrayed the cost of this investigation.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

CLV.—*Chlorination of Acylanilides. Effect of the Constitution of the Acyl Group on the Proportion of the Ortho- and Para-derivatives.*

By HAROLD KING and KENNEDY JOSEPH PREVITÉ ORTON.

IN a previous paper, Jones and Orton (Trans., 1909, **95**, 1056) demonstrated that in the chlorination of acetanilide about 40—46 per cent. of the product was *o*-chloro- and 54—60 per cent. *p*-chloroacetanilide. This ratio appeared to be independent of the dilution of the acetic acid which was used as solvent, a fact which implies only that the rates of the formation of the two chloro-derivatives bear the same relation to one another in such media.

In this paper we record the effect of varying the acyl group on the proportion of *o*- and *p*-chloro-derivative, and have used form-, propion-, stear-, and benz-anilide.

As the medium, acetic acid, more or less diluted, is alone suitable, for in other (anhydrous) media, chloroform and so forth, considerable quantities of a dichloro-derivative are produced, and consequently a part of the original anilide left unchanged. The cause of this difference is not to be found in a similarity in the velocities of chlorination of unsubstituted anilide and monochloroanilide; the chlorination of the unsubstituted anilide is some two hundred times as fast as that of the *p*-chloro-derivative, which is three to four times as rapid as the chlorination of the *o*-derivative. It is more probable that the formation of the dichloro-derivative is due to the preferential combination of the hydrogen chloride with the unsubstituted anilide, which is thus shielded from the attack of chlorine.

The results are summarised in the following table, where the numbers represent the percentage of the anilide chlorinated, found in the product in one or other form.

	p-Chloro-anilide.	*o*-Chloro-anilide.	Ratio: *o*-Chloroanilide, *p*-Chloroanilide.	2 : 4-Dichloro-anilide.	Unchanged anilide.
Acetanilide ...	51·0	44	0·89/1	1·2	1·2
Propionanilide	64	26	0·4/1	3·2	3·2
Stearanilide ...	69·5	20·8	0·3/1	2·2	2·2
Benzanilide ...	65·5	11·2	0·17/1	11·1	9·2
Formanilide ...	62	3·0	0·048/1	—	—

The loss which is apparent from these figures is to be attributed mainly to the difficulty of estimating with any accuracy the amount of anilide which escapes chlorination.

In the case of formanilide some other reaction takes place simultaneously, which is the more prominent in dilute acetic acid solution, when as much as 75 per cent. of the anilide escapes chlorination; the figures given are for glacial acetic acid.

The *p*-chloroanilide bears the greater proportion of the loss which results from the formation of the dichloro-derivative, since, apart from its greater concentration, the speed of chlorination of the *p*-chloro-compound is two to four times as great as that of the *o*-chloro-compound. Hence the figures for the *p*-chloro-compound are all relatively low.

The numbers in the fourth column express the ratio of the velocities of the formation of the two monochloroanilides. They appear to be independent of the dilution of the acetic acid. It is obvious that the chlorination of acetanilide is the most favourable process for the production of *o*-chloroaniline. The figures show the remarkable position occupied by formanilide; the *o*-chloro-derivative is only formed at 1/20th the rate of the para-derivative.

Omitting formanilide, the effect of the nature of the acyl group on the proportion of the two derivatives belongs to the general "steric" type met with in similar reactions.

Experimental.

The method of estimating the proportion of *o*- and *p*-chloroacylanilides is generally the same as that used for acetanilide by Jones and Orton (*loc. cit.*). A solution of anilide in glacial acetic acid is treated with that quantity of bleaching powder solution which will give one molecular proportion of chlorine. The solid which separates is collected, and when possible the proportion of *o*- and *p*-chloro-derivatives estimated from the melting point. A second separation is obtained by dilution to 20 or 10 per cent. acetic acid. This last mother liquor, which often contains much of the ortho-

derivative, is either strongly acidified, boiled to hydrolyse the anilide, and then, after removal of the mineral acid with alkali or sodium acetate, distilled in steam, when the anilines pass over; or it is extracted with chloroform, and the anilide thus obtained hydrolysed with aqueous sulphuric acid.

The different chloroanilines are separated by distilling from 1 per cent. sulphuric acid, when the *o*-chloro- and the 2:4-dichloro-compounds pass over, leaving *p*-chloroaniline and aniline in the acid mother liquor. They are subsequently distilled, after rendering the liquid alkaline. The *o*- and *p*-chloroacylanilide in the separations from the original acetic acid liquors are treated in the same way, when the melting-point curve of the mixture is not available for the estimation.

The 2:4-dichloroaniline is separated from the *o*-chloro-compound by fractional precipitation from solutions of the hydrochlorides as previously described (*loc. cit.*). For weighing, it is generally simplest to convert the anilines into acetyl derivatives by evaporation on the water-bath with a little acetic anhydride in tared glass dishes. In the following, some of the final and more successful experimental results are given.

Formanilide:—Treatment of the glacial acetic acid solution with bleaching powder solution produced a coloured liquid, which darkened on warming. Only 25 per cent. of the anilide could be recovered by the method above described.

The loss was greatly decreased (to 25 per cent.) when the anilide was treated with a standard solution of chlorine in glacial acetic acid. After neutralising with sodium carbonate, the acetic acid was completely distilled off under diminished pressure. The remaining anilides were hydrolysed, and the anilines separated.

Propionanilide:—Ten grams of propionanilide in 150 c.c. of glacial acetic acid were treated with one equivalent of bleaching powder solution, and finally diluted to 10 per cent. acetic acid, when 6·8 grams separated. Extraction with chloroform yielded an additional 6·5 grams. The total solid was hydrolysed, and the anilines separated with the following result:

Propionanilide recovered as *p*-chloroacetanilide	6·4 grams
,, ,, ,, *o*-chloroacetanilide	2·57 ,,
,, ,, ,, 2:4-dichloroacetanilide	0·32 ,,
,, ,, ,, acetanilide	0·32 ,,
Loss	0·39 ,,

Benzanilide:—Owing to the sparing solubility, 500 c.c. were required for 10 grams. The main quantity of chlorinated anilides separated on dilution to 50 per cent., and the proportion of *o*- and *p*-chloro-derivatives was estimated from the melting-point curve. The

material remaining in solution was recovered and analysed as described in the foregoing.

Benzanilide recovered as *p*-chloroacetanilide	6·54	grams
,, ,, ,, *o*-chloroacetanilide	1·11	,,
,, ,, ,, 2 : 4-dichloroacetanilide	1·11	,,
,, ,, ,, acetanilide	0·92	,,
Loss	0·32	,,

Stearanilide:—The anilide, which was prepared by heating stearic acid with excess of aniline at 280—300° for five hours, is so sparingly soluble that 600 c.c. of glacial acetic acid are required for 5 grams at 40°. The separation of unchlorinated anilide during the addition of the bleaching powder can be avoided by using a concentrated solution of the latter. There was some difficulty experienced in hydrolysing the anilides, many hours' boiling with aqueous alcoholic sulphuric acid being necessary.

Neither *o*- nor *p*-chlorostearanilide has hitherto been described. Two grams of stearanilide dissolved in 300 c.c. of glacial acetic acid were treated with the calculated quantity of concentrated bleaching powder solution. A solid separated, which melted at 94—99°. Repeated crystallisation from acetic acid raised the melting point to 101—102°. p-*Chlorostearanilide* forms feathery needles, which gave on analysis the following numbers:

0·2760 gave 0·0978 AgCl. Cl = 8·8.

$C_{24}H_{40}ONCl$ requires Cl = 9·0 per cent.

On hydrolysis, *p*-chloroaniline was obtained.

The mother liquor from the above was diluted to 50 per cent. acetic acid, whereupon a solid, melting at 60—65°, separated. Repeated crystallisation from alcohol raised the melting point to 67—68·5°. o-*Chlorostearanilide* forms needles:

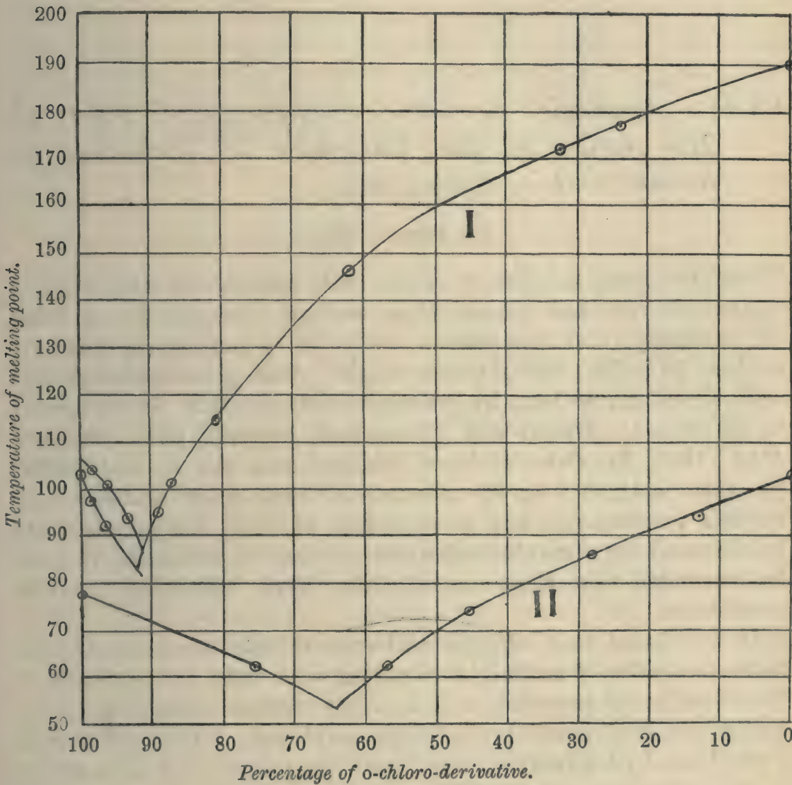
0·2082 gave 0·737 AgCl. Cl = 8·8 per cent.

$C_{24}H_{40}ONCl$ requires Cl = 9·0 per cent.

Preparation of o-*Chloroaniline:*—As a result of our experience, we find that *o*-chloroaniline is best prepared and purified in the following way. One hundred grams of acetanilide dissolved in 1 litre of glacial acetic acid are treated with one equivalent of bleaching powder solution. After keeping for fifty hours, the solid is collected, and recrystallised once more from alcohol, 50 grams of pure *p*-chloroacetanilide being obtained.

The alcoholic and acetic acid mother liquors contain the *o*-chloroacetanilide, together with 5—10 per cent. of the *p*-chloro-compound. The alcoholic mother liquor is evaporated to dryness, and the acetic acid liquor diluted to 5 per cent., and extracted with chloroform. The mixed solids are hydrolysed with 10 per cent.

aqueous sulphuric acid, and the solution diluted to 1 per cent. acid and distilled in steam. The *o*-chloroaniline which passes over, with a small quantity of the para-compound, is collected with chloroform, and dissolved in warm 10 per cent. hydrochloric acid, using 11 c.c. of acid for each gram of *o*-chloroaniline. The hydrochloride of the *o*-chloro-derivative separates on cooling, and can be again recrystallised in the same way. The purity can be tested by the



melting point of the acetyl derivative. In this way a far better yield of purer material can be obtained than by crystallisation of the picrate from alcohol or the acetyl derivative from petroleum.

Melting-point Curves of Mixtures of o- *and* p-*Chlorobenz- and* o- *and* p-*Chloroform-anilides.*

The figure shows the form of the two curves: I is benzanilide, and II formanilide. As in the case of the corresponding acet-

anilides (Jones and Orton, *loc. cit.*), it will be seen that a part of the chlorobenzanilide curves is duplicated; here, however, it occurs when the *o*-chloro-derivative is in excess, whereas in the case of the acetyl derivatives the *p*-chloro-compound was in excess.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

CLVI.—*Aromatic Antimony Compounds. Part II. The Action of the Chlorides of Antimony on Aniline and its Derivatives.*

By PERCY MAY.

WHEN antimony trichloride reacts with aniline, the only organic compounds obtained contain three aromatic residues to one atom of antimony, and compounds such as *p*-aminophenyldichlorostibine, $NH_2{\cdot}C_6H_4{\cdot}SbCl_2$, which might yield *p*-aminophenylstibic acid, $NH_2{\cdot}C_6H_4{\cdot}SbO_3H_2$, by hydrolysis and oxidation, do not appear to be formed. Breinl and Nierenstein, however (*Ann. Tropical Med.*, 1909, **2**), claim to have obtained both the *m*- and *p*-acids by this method. As the account of their work contains very obvious inaccuracies, and as no traces of these compounds could be obtained by a careful repetition of their experiments, it must be concluded that these investigators were mistaken in their conclusions.

It was found that whereas antimony trichloride combines with three molecules of aniline, it combines with only one molecule of toluidine or chloroaniline, and does not combine with nitroaniline under the experimental conditions employed. The compounds formed are hydrolysed by water, and are probably of an additive nature. The structure $Sb(C_6H_4{\cdot}NH_2,HCl)_3$ is unlikely, for although the entrance of an amino-group into each aromatic radicle would probably reduce the stability of triphenylstibine, yet the latter is so very stable (Trans., 1910, **97**, 1956) that it is improbable that the amino-derivative would be so readily hydrolysed. On the other hand, the mono-aryl derivatives, such as $C_6H_5{\cdot}SbCl_2$, are less stable, and this fact, together with the somewhat greater stability of the derivatives of toluidine compared with those of aniline, renders it possible that the former may have the structure:

$$SbCl_2{\cdot}C_6H_3Me{\cdot}NH_2,HCl.$$

By heating aniline and antimony trichloride at a higher temperature, a substance is formed having the composition

$$SbCl_3,(C_6H_5\cdot NH_2)_3,2HCl.$$

This compound is somewhat more stable than the compound $SbCl_3,(C_6H_5\cdot NH_2)_3$, obtained at a lower temperature, although it decomposes into antimony chloride and aniline hydrochloride when it is warmed with hydrochloric acid.

Antimony pentachloride reacts violently with most aromatic compounds. In all the cases that have been investigated, partial chlorination of the aromatic compound takes place, the remainder then forming additive products with the antimony trichloride set free. This explains the value of antimony trichloride as a catalytic agent in the chlorination of organic compounds.

Experimental.

Action of Antimony Trichloride on Aniline.

On mixing equal quantities of aniline and antimony trichloride, heat is evolved, and combination ensues. The compound formed is readily soluble in hot aniline, from which, on cooling, it crystallises in needles. If the excess of aniline is removed by washing with an inert solvent, such as ether or light petroleum, the crystals are destroyed, and therefore these appear to contain aniline of crystallisation.

This compound was obtained in the pure state by the following method. Sixteen grams of aniline were warmed on the water-bath with 10 grams of antimony trichloride for a quarter of an hour; the product was extracted with hot benzene, and the solution filtered. The residue was washed with alcohol, and dried in a vacuum (I), and from the filtrate white needles separated, which were dried on a porous plate and then in a vacuum (II).

The antimony was estimated by dissolving in hydrochloric acid, and precipitating as sulphide in the usual way. The chlorine, except where otherwise indicated, was estimated by boiling with dilute nitric acid and excess of standard silver nitrate, the excess of silver being then determined by means of thiocyanate.

Crops I and II were found to have the same composition:

Found: Sb = 23·79, 23·80; Cl = 21·13.

$SbCl_3,(C_6H_5\cdot NH_2)_3$ requires Sb = 23·76; Cl = 21·00 per cent.

This substance could be obtained more readily by adding a slight excess of aniline to a solution of antimony trichloride in benzene until the precipitate first formed just redissolved. Part of the solvent was evaporated, and the solid residue separated and extracted with light petroleum to remove all free aniline. The

white product thus obtained was recrystallised from alcohol, and obtained in needles. (Found: Sb = 23·53; Cl = 21·4.)

Trianiline antimony trichloride melts and decomposes at 130—170° (Schiff, *Ber.*, 1901, **34**, 805, gives 80°), is hydrolysed by water or alkali, and dissolves readily in hydrochloric acid, less readily in other mineral acids, giving the reactions of the corresponding salts of aniline and of antimony.

On boiling with 90 per cent. alcohol and filtering, the filtrate, on evaporation, yielded crystals of aniline hydrochloride, which were identified by analysis and by their melting point, indicating that the substance had been hydrolysed under these conditions. Aqueous ammonium carbonate decomposes the substance, with liberation of aniline and antimony trioxide.

Action of Aniline on Antimony Trichloride at a Higher Temperature.

Forty grams of antimony trichloride were heated to 210°, and 40 grams of aniline added in small portions at a time, the mixture being kept boiling for half an hour. When cooled to about 80°, the product was poured into cold water, and the purple precipitate collected, washed, and extracted with alcohol. From the alcoholic extract almost colourless crystals were obtained, which dissolved in hydrochloric acid, giving solutions which could be diazotised, and which gave an orange precipitate with hydrogen sulphide. The substance behaves, therefore, like an additive product of antimony trichloride and aniline:

0·1495 gave 0·2063 CO_2 and 0·0651 H_2O. C = 37·62; H = 4·35.
0·1760 „ 0·2146 AgCl; Cl = 30·94.

$SbCl_3,(C_6H_5{\cdot}NH_2)_3,2HCl$ requires C = 37·3; H = 4·0; Cl = 30·65 per cent.

This compound forms colourless crystals, which dissolve in hot alcohol, and are insoluble in, and almost unchanged by, water. They melt and decompose at 170—175°.

Action of Antimony Trichloride on o-*Toluidine.*

o-Toluidine was added to a benzene solution of antimony trichloride, and the product treated in just the same way as described in the case of aniline:

Found: Cl = 31·95, 31·56; N = 4·88.

$SbCl_3,C_6H_4Me{\cdot}NH_2$ requires Cl = 31·84; N = 4·20 per cent.

o-Toluidine antimony trichloride crystallises from alcohol in long, colourless needles, which melt sharply at 148°, without any decom-

position. It resembles trianiline antimony trichloride in its behaviour towards hydrochloric acid, nitrous acid, and ammonium carbonate. It is not, however, hydrolysed by boiling with 90 per cent. alcohol.

Compound of p-*Toluidine and Antimony Trichloride.*

This compound was prepared in the same manner as that derived from *o*-toluidine, which it resembles in its chemical character, but does not crystallise so well, and does not melt without decomposition.

p-*Toluidine antimony trichloride* forms colourless crystals, which decompose above 120°:

Found: Cl = 31·12; N = 4·42.

$SbCl_3,C_6H_4Me\cdot NH_2$ requires Cl = 31·84; N = 4·20 per cent.

Compound of p-*Chloroaniline and Antimony Trichloride.*

On mixing benzene solutions of antimony trichloride and *p*-chloroaniline, a precipitate was formed, which did not redissolve in excess of either of the reagents. The precipitate was collected, and washed with benzene and alcohol, in both of which solvents it is practically insoluble:

Found: N = 3·49; Cl(ionisable) = 31·0.

$SbCl_3,C_6H_4Cl\cdot NH_2$ requires Cl = 30·2(ionisable); N = 3·98 per cent.

p-*Chloroaniline antimony trichloride* is a white powder, practically insoluble in all the usual organic solvents, and melts with some decomposition at 160—165°. In its chemical behaviour it resembles the corresponding toluidine derivatives.

m-Nitroaniline and *p*-nitroaniline do not combine with antimony trichloride under the above-described experimental conditions.

The Action of Antimony Pentachloride on Benzene, Aniline, etc.

The action of antimony pentachloride on benzene is very violent. Charring takes place, hydrogen chloride is evolved, and crystals of an additive compound separate; the action of antimony pentachloride on toluene and xylene is similar. In the case of aniline the action is almost explosive in its violence, and is best controlled by dissolving both the reacting substances in chloroform, one of the few organic solvents with which antimony pentachloride does not vigorously react. Even then, on slowly adding a chloroform solution of antimony pentachloride to one of aniline, the reaction is very vigorous, and so much charring takes place that it was not possible to isolate any compound in a pure condition. A chloroform solution of antimony pentachloride on evaporation leaves crystals

of an additive compound, which was too unstable for analysis, losing chloroform when the vapour pressure of the latter falls below a certain point. When exposed to moist air it gave the vitreous antimonic oxychloride described by Anschütz and Evans.

I wish to express my thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed most of the expenses of this investigation.

UNIVERSITY COLLEGE, LONDON.

CLVII.—*The Synthesis of Histidine.*

By FRANK LEE PYMAN.

IN the following paper an account is given of the synthesis of histidine (*l*-α-amino-β-glyoxaline-4(or 5)-propionic acid), and it may be of interest, in the first place, to recall that this amino-acid is

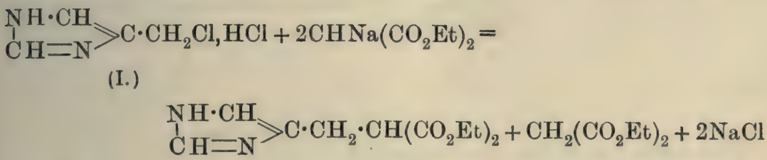
$$\begin{matrix} NH\cdot CH \\ | \\ CH{=}N \end{matrix}\!\!>\!C\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,$$

Histidine.

a compound of considerable biochemical importance, since it occurs as a degradation product of nearly all albumins, and notably in large amount by the hydrolysis of hæmoglobin. It was first discovered by Kossel (*Zeitsch. physiol. Chem.*, 1896, **22**, 176), and its constitution was determined mainly by the work of Fränkel (*Monatsh.*, 1903, **24**, 229), Paul (*Zeitsch. physiol. Chem.*, 1904, **42**, 513), and Knoop and Windaus (*Beitr. chem. Physiol. Path.*, 1905, **7**, 144).

In a recent communication (this vol., p. 668) the preparation of certain glyoxaline derivatives was described. It was shown that 4(or 5)-chloromethylglyoxaline (I) is a highly reactive compound, the chlorine atom in the side-chain being readily replaced by hydroxyl under the influence of hot water, and by the cyano-group through the agency of aqueous potassium cyanide at 0°. It therefore seemed probable that this salt could be condensed with compounds of the type of ethyl sodiomalonate, forming the corresponding glyoxalinemethyl, $C_3H_3N_2\cdot CH_2\cdot$, derivatives, and this proved to be the case. On adding one molecule of this salt to two molecules of ethyl sodiomalonate, *ethyl* 4(or 5)-*glyoxalinemethylmalonate*

(II) was formed in a yield amounting to 49 per cent. of the theoretical:

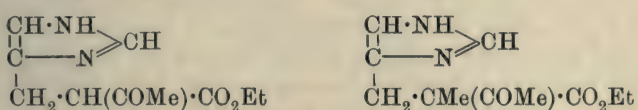


(I.) (II.)

This ester, on hydrolysis with barium hydroxide, gave the corresponding acid, 4(or 5)-*glyoxalinemethylmalonic acid* (III), together with a certain amount of β-glyoxaline-4(or 5)-propionic acid (IV), produced from the former by the removal of carbon dioxide. 4(or 5)-Glyoxalinemethylmalonic acid is a beautifully crystalline compound, which, on heating, loses carbon dioxide at 180°, and is converted into β-glyoxaline-4(or 5)-propionic acid (IV), a substance which has previously been prepared by Knoop and Windaus (*Beitr. chem. Physiol. Path.*, 1905, **7**, 144), both by the degradation of histidine, and synthetically from glyoxylpropionic acid:

(III.) (IV.)

Similar condensation products were obtained by the action of 4(or 5)-chloromethylglyoxaline hydrochloride on ethyl sodioacetoacetate and ethyl sodiomethylacetoacetate, *ethyl* 4(or 5)-*glyoxalinemethylacetoacetate* (V) and *ethyl* 4(or 5)-*glyoxalinemethylmethylacetoacetate* (VI) being formed:

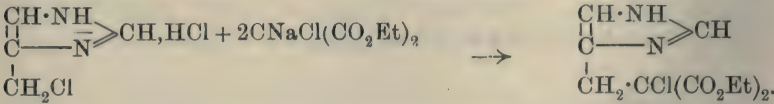


(V.) (VI.)

In view of these results, it seemed of interest to attempt the condensation of this salt with ethyl sodiochloromalonate, since this might lead to a synthesis of histidine, for Conrad (*Annalen*, 1881, **209**, 241) has shown that this ester condenses with benzyl chloride, forming ethyl benzylchloromalonate, although it does not condense with less reactive alkyl chlorides.

On experiment, it was found that 4(or 5)-chloromethylglyoxaline hydrochloride readily condenses with ethyl sodiochloromalonate,

forming *ethyl* 4(or 5)-*glyoxalinemethylchloromalonate* (VII) in a yield amounting to 60 per cent. of the theoretical:



(VII.)

This ester is readily hydrolysed by boiling 20 per cent. hydrochloric acid, losing two molecules of ethyl alcohol and one of carbon dioxide, and thus becoming almost quantitatively converted into r-*α-chloro-β-glyoxaline*-4(or 5)-*propionic acid* (VIII). This acid, when heated with concentrated aqueous ammonia at 110°, yields r-*α-amino-β-glyoxaline*-4(or 5)-*propionic acid* (IX), that is, *r*-histidine, in a yield amounting to 38 per cent. of the theoretical:

(VIII.) (IX.)

The identity of this synthetic *r*-histidine with that obtained by racemising the naturally occurring lævo-variety (Fränkel, *Beitr. chem. Physiol. Path.*, 1906, **8**, 156; Ewins and Pyman, this vol., p. 339) has been established by analyses of the base and two salts, and by the agreements in the melting points of the base and four salts from either source and the respective mixtures.

The synthesis of histidine itself, that is, the naturally occurring lævo-modification, has been completed by the resolution of the racemic variety. When equimolecular amounts of *r*-histidine and *d*-tartaric acid were crystallised from water, there separated first d-*histidine* d-*hydrogen tartrate* (melting point 234° (corr.); $[\alpha]_D + 13{\cdot}3°$). This salt is sparingly soluble in water, and is obtained in a yield amounting to about 90 per cent. of the theoretical. The hitherto unknown d-*histidine* was regenerated from it, and found to melt at 287—288° (corr.), and to have $[\alpha]_D + 39{\cdot}3°$. The mother liquors from the *d*-base-*d*-acid then deposited the easily soluble but magnificently crystalline l-*histidine* d-*hydrogen tartrate* (melting point 172—173° (corr.); $[\alpha]_D + 17{\cdot}4°$) in a yield amounting to nearly 80 per cent. of the theoretical. The *l*-histidine regenerated from this was found to have $[\alpha]_D - 36{\cdot}6°$, and was therefore further purified by conversion into the sparingly soluble l-*histidine* l-*hydrogen tartrate* (melting point 234° (corr.); $[\alpha]_D - 12{\cdot}1°$). After regeneration from this salt, *l*-histidine melted at 287—288° (corr.), and had $[\alpha]_D - 38{\cdot}1°$.

The specific rotatory power is thus substantially in agreement

with that found for natural histidine, $[\alpha]_D -39{\cdot}7°$ by Kossel and Kutscher (*Zeitsch. physiol. Chem.*, 1899, **28**, 382).

The following scheme shows the steps by which the synthesis of histidine has been effected:

Citric acid.

↓

Acetonedicarboxylic acid.

↓

Di*iso*nitrosoacetone.

↓

Diaminoacetone hydrochloride.

↓

2-Thiol-4(or 5)-aminomethylglyoxaline.

↓

4(or 5)-Hydroxymethylglyoxaline.

↓

4(or 5)-Chloromethylglyoxaline hydrochloride.

↓

Ethyl 4(or 5)-glyoxalinemethylchloromalonate.

↓

r-α-Chloro-β-glyoxaline-4(or 5)-propionic acid.

↓

r-Histidine.

↓

l-Histidine.

There are a few other points of interest about some of the compounds described. It has already been stated that ethyl 4(or 5)-glyoxalinemethylchloromalonate yields *r*-α-chloro-β-glyoxaline-4(or 5)-propionic acid on hydrolysis with acid, and it was thought that this ester would give the corresponding tartronic acid (X) when boiled with alkali:

(X.)

This, however, was not the case, boiling dilute aqueous sodium hydroxide eliminating one of the nitrogen atoms of the glyoxaline nucleus in the form of ammonia. This remarkable reaction has not yet been further studied, but one other case of a glyoxaline derivative behaving similarly is described in the literature. Thus, Pinner (*Ber.*, 1905, **38**, 2560) found that metapilocarpine—an isomeride of

pilocarpine obtained from the hydrochloride of the latter by prolonged heating at a high temperature—lost half its nitrogen as methylamine when boiled with aqueous potassium hydroxide, nitrogenous acids being produced at the same time. Normally, the glyoxaline ring is quite unaffected by boiling alkalis, except in the case of its quaternary salts, which lose both atoms of nitrogen as the corresponding alkylamines (compare Pinner and Schwarz, *Ber.*, 1902, **35**, 2446).

Ethyl 4(or 5)-glyoxalinemethylchloromalonate gave, with cold alcoholic ammonia, 4(or 5)-*glyoxalinemethylchloromalonamide* (XI), which was isolated in the form of its hydrochloride; strong

$$\begin{matrix} NH\cdot CH \\ | \\ CH{=}N \end{matrix}\!\!>\!C\cdot CH_2\cdot CCl(CO\cdot NH_2)_2$$

(XI.)

ammonia at 110°, however, gave an uninviting product, which was neglected.

It should be mentioned that the *r*-α-chloro-β-glyoxaline-4(or 5)-propionic acid mentioned above melts at 201° (corr.), that is, 10° higher than the α-chloro-β-glyoxaline-4(or 5)-propionic acid described by Windaus and Vogt (*Beitr. chem. Physiol. Path.*, 1908, **11**, 406). The latter, however, was prepared from *l*-histidine, and is doubtless the corresponding optically active variety.

r-α-*Hydroxy-β-glyoxaline*-4(or 5)-*propionic acid* (XII) has also been prepared by the action of hot moist silver oxide on *r*-α-chloro-

$$\begin{matrix} NH\cdot CH \\ | \\ CH{=}N \end{matrix}\!\!>\!C\cdot CH_2\cdot CH(OH)\cdot CO_2H$$

(XII.)

β-glyoxaline-4(or 5)-propionic acid. It melts at 222° (corr.), thus differing from the "oxydeaminohistidine," that is, α-hydroxy-β-glyoxaline-4(or 5)-propionic acid, melting at 204°, prepared by Fränkel (*Monatsh.*, 1903, **24**, 229) by the action of silver nitrite on *l*-histidine. Here again the difference lies, no doubt, in the optical activity of the acid obtained from the natural product. Both acids crystallise with one molecule of water of crystallisation.

Experimental.

Ethyl 4(or 5)-*Glyoxalinemethylmalonate*,

$$\begin{matrix} NH\cdot CH \\ | \\ CH{=}N \end{matrix}\!\!>\!C\cdot CH_2\cdot CH(CO_2Et)_2.$$

Twenty grams of 4(or 5)-chloromethylglyoxaline hydrochloride were brought into reaction with two molecular proportions of ethyl sodiomalonate, and the product worked up in the same way as that from ethyl sodiochloromalonate (p. 1392); the yield was 21 grams

of *ethyl* 4(or 5)-*glyoxalinemethylmalonate hydrogen oxalate*, that is, 49 per cent. of the theoretical.

Ethyl 4(or 5)-*glyoxalinemethylmalonate hydrogen oxalate* crystallises from water in large, hard, clear, nearly rectangular, oblong plates, which melt at 155—158° (corr.). It is anhydrous, sparingly soluble in cold, but readily so in hot, water:

0·1488 gave 0·2564 CO_2 and 0·0727 H_2O. C=47·0; H=5·5.
0·1413 „ 10·6 c.c. N_2 at 19° and 778 mm. N=9·0.
$C_{11}H_{16}O_4N_2,C_2H_2O_4$ requires C=47·2; H=5·5; N=8·5 per cent.

The base was regenerated from the oxalate by means of sodium carbonate and ether; after distillation of the solvent, it remained as a yellow oil, which became very viscid when cold, but readily poured when warm. It showed no signs of crystallisation after long keeping. It is sparingly soluble in water, but readily so in alcohol or ether.

The *hydrochloride* occurs as a deliquescent mass of needles, melting indefinitely at 50—70°, and readily soluble in water, alcohol, acetone, or ethyl acetate.

The *hydriodide* is a crystalline salt of similar properties.

4(or 5)-*Glyoxalinemethylmalonic Acid*,

$$\begin{matrix}NH\cdot CH\\ |\\ CH{=}N\end{matrix}\!\!>\!C\cdot CH_2\cdot CH(CO_2H)_2.$$

Ethyl 4(or 5)-glyoxalinemethylmalonate was boiled with an excess of baryta water for several hours; a stream of carbon dioxide was then led through the liquid, and the barium carbonate removed by filtration. The clear filtrate, containing the barium salts of 4(or 5)-glyoxalinemethylmalonic acid and β-glyoxaline-4(or 5)-propionic acid, was then made up to a known volume, and the barium in an aliquot portion determined.

The liquor was then treated with a quantity of oxalic acid exactly sufficient to remove the barium, filtered from barium oxalate, and concentrated to low bulk, when 4(or 5)-glyoxalinemethylmalonic acid crystallised out on cooling; the mother liquor contained β-glyoxaline-4(or 5)-propionic acid.

4(or 5)-*Glyoxalinemethylmalonic acid* crystallises from water in beautiful, clear, hexagonal plates. It is easily soluble in hot water, but sparingly so in cold water or alcohol:

0·1512 gave 0·2530 CO_2 and 0·0596 H_2O. C=45·6; H=4·4.
$C_7H_8O_4N_2$ requires C=45·6; H=4·4 per cent.

When heated, this malonic acid melts and effervesces at 180° (corr.), losing carbon dioxide; it resolidifies while still hot, and does not then melt until 207° (corr.), β-glyoxaline-4(or 5)-propionic acid,

$C_3H_3N_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, being formed. A quantity of the latter acid was prepared in this manner, and after recrystallisation from water melted at 209—210° (corr.). (Found, C = 51·1; H = 6·0. Calc., C = 51·4; H = 5·8 per cent.) Knoop and Windaus, who have previously prepared this acid in other ways (*Beitr. chem. Physiol. Path.*, 1905, **7**, 144), give m. p. 208—209°.

Ethyl 4(or 5)-*Glyoxalinemethylacetoacetate*, $C_3H_3N_2 \cdot CH_2 \cdot CH(COMe) \cdot CO_2Et$.

This compound was prepared by condensing 4(or 5)-chloromethylglyoxaline hydrochloride (1 mol.) with ethyl sodioacetoacetate (2 mols.).

The *hydrogen oxalate* crystallises from water in rosettes of thin, clear plates, which melt and decompose at 145—146° (corr.). It is anhydrous, fairly readily soluble in cold water, and easily so in hot:

0·1535 gave 0·2704 CO_2 and 0·0751 H_2O. C = 48·0; H = 5·5.
0·1148 ,, 9·3 c.c. N_2 at 17° and 754 mm. N = 9·5.
$C_{10}H_{14}O_3N_2,C_2H_2O_4$ requires C = 48·0; H = 5·3; N = 9·3 per cent.

Ethyl 4(or 5)-*Glyoxalinemethylmethylacetoacetate*, $C_3H_3N_2 \cdot CH_2 \cdot CMe(COMe) \cdot CO_2Et$.

This compound was prepared by condensing 4(or 5)-chloromethylglyoxaline hydrochloride (1 mol.) with ethyl sodiomethylacetoacetate (2 mols.).

The *hydrogen oxalate* crystallises from water in clusters of beautiful, clear, glistening plates, which melt and decompose at 155—156° (corr.). It is anhydrous, fairly readily soluble in cold water, and easily so in hot:

0·1525 gave 0·2874 CO_2 and 0·0823 H_2O. C = 51·4; H = 6·1.
0·1300 ,, 10·2 c.c. N_2 at 18° and 762 mm. N = 9·2.
$(C_{11}H_{16}O_3N_2)_4,(C_2H_2O_4)_3$ requires C = 51·4; H = 6·1; N = 9·6 per cent.

On regenerating the base, dissolving it in absolute alcoholic hydrogen chloride, and evaporating nearly to dryness in an evacuated desiccator, a crystalline *hydrochloride* separated in deliquescent needles, which were very easily soluble in water, alcohol, acetone, or ethyl acetate.

Ethyl 4(or 5)-*Glyoxalinemethylchloromalonate*,

$$\begin{array}{l} NH \cdot CH \\ | \\ CH{=}N \end{array} \!\!> C \cdot CH_2 \cdot CCl(CO_2Et)_2.$$

To 9·2 grams of sodium, dissolved in 200 c.c. of absolute alcohol, 78 grams of ethyl chloromalonate were added, followed by a solution

of 30·6 grams of 4(or 5)-chloromethylglyoxaline hydrochloride in 150 c.c. of absolute alcohol, the liquid being kept cold during both additions. The mixture was then boiled for one and a-half hours under a reflux condenser, filtered from sodium chloride, and the solvent removed by distillation. The resulting oil was mixed with dilute hydrochloric acid, and extracted with ether to remove the non-basic esters; the liquor was then rendered alkaline with sodium carbonate, and completely extracted with ether. The residue, after evaporation of the solvent, consisting of a clear, brown oil, was dissolved in a solution of 25 grams of oxalic acid in 550 c.c. of boiling water, and decolorised with animal charcoal. On cooling, 39 grams of pure *ethyl* 4(or 5)-*glyoxalinemethyl chloromalonate hydrogen oxalate* separated, and further small quantities (about 3 grams) were obtained from the mother liquors, the yield thus amounting to 60 per cent. of the theoretical.

Ethyl 4(or 5)-*glyoxalinemethylchloromalonate hydrogen oxalate* crystallises from water in shimmering leaflets, which melt and decompose at 176° (corr.). This salt is sparingly soluble in cold water, but readily so in hot. It is anhydrous:

0·1517 gave 0·2442 CO_2 and 0·0647 H_2O. C=43·9; H=4·8.
0·1507 „ 0·2415 CO_2 „ 0·0635 H_2O. C=43·7; H=4·7.
0·2315 „ 0·0991 AgCl. Cl=10·6.

$(C_{11}H_{15}O_4N_2Cl)_4,(C_2H_2O_4)_3$ requires C=43·8; H=4·8; Cl=10·4 per cent.

The *hydrochloride* crystallises from acetone in beautiful, large, glistening, diamond-shaped plates, which melt at 148—149° (corr.). It is anhydrous, readily soluble in water or alcohol, fairly readily so in hot acetone, and sparingly so in cold acetone:

0·1556 gave 0·2423 CO_2 and 0·0739 H_2O. C=42·5; H=5·3.

$C_{11}H_{15}O_4N_2Cl,HCl$ requires C=42·4; H=5·2 per cent.

Aqueous solutions of the hydrochloride give a sparingly soluble precipitate with picric acid or Meyer's solution, and give a deep red coloration with sodium diazobenzene-*p*-sulphonate in alkaline solution. The free base was regenerated by shaking the salts with sodium carbonate and ether; it formed a viscid oil which did not crystallise, and is easily soluble in alcohol, ether, or chloroform, but very sparingly so in water.

Ethyl 4(or 5)-glyoxalinemethylchloromalonate yields, on hydrolysis with 20 per cent. hydrochloric acid, *r*-α-chloro-β-glyoxaline-4(or 5)-propionic acid. When hydrolysed by boiling with dilute aqueous sodium hydroxide, however, it loses half its nitrogen as ammonia. This was determined quantitatively by absorption in dilute sulphuric acid in the usual way.

0·2532 (oxalate) gave NH_3 requiring 7·4 c.c. $N/10$-H_2SO_4; N = 4·1.

0·5008 (oxalate) gave NH_3 requiring 15·2 c.c. $N/10$-H_2SO_4; N = 4·3.

$(C_{11}H_{15}O_4N_2Cl)_4,(C_2H_2O_4)_3$ requires total N = 8·2 per cent.

With cold ammonia, it yields 4(or 5)-glyoxalinemethylchloromalonamide, but with strong ammonia at 110° only dark brown, uninviting products are obtained.

*r-α-Chloro-β-glyoxaline-*4(or 5)*-propionic Acid,*

$$\left.\begin{array}{l} NH\cdot CH \\ | \\ CH{=\!=}N \end{array}\right> C\cdot CH_2\cdot CHCl\cdot CO_2H.$$

Ten grams of ethyl 4(or 5)-glyoxalinemethylchloromalonate hydrochloride were boiled with 100 c.c. of 20 per cent. hydrochloric acid for forty-five minutes. The liquor was evaporated to dryness under diminished pressure, moistened with water, and again evaporated to dryness. The resulting colourless varnish was dissolved in 300 c.c. of cold water, digested cold with the silver carbonate from 8 grams of silver nitrate, filtered from silver chloride, and treated with hydrogen sulphide. After the removal of silver sulphide, the filtrate was evaporated to low bulk under diminished pressure, and allowed to crystallise, when 5·1 grams of pure *r*-α-chloro-β-glyoxaline-4(or 5)-propionic acid were obtained; this yield represents 91 per cent. of the theoretical.

r-α-*Chloro-β-glyoxaline-*4(or 5)*-propionic acid* crystallises from water in white, star-like clusters of prismatic needles. It is anhydrous, and melts and decomposes at 201° (corr.), but the melting point varies considerably with the rate of heating, and may be found anywhere between 198° and 204° (corr.). It is sparingly soluble in cold water, alcohol, or acetone, but readily so in hot water:

0·1547 gave 0·2334 CO_2 and 0·0571 H_2O. C = 41·1; H = 4·1.

0·1604 „ 0·1319 AgCl. Cl = 20·3.

$C_6H_7O_2N_2Cl$ requires C = 41·3; H = 4·1; Cl = 20·3 per cent.

The α-chloro-β-glyoxaline-4(or 5)-propionic acid previously described by Windaus and Vogt (*Beitr. chem. Physiol. Path.*, 1908, **11**, 406) is stated to melt at 191°; it is doubtlessly the optically active variety corresponding with *l*-histidine, from which it was prepared.

Synthesis of r-*Histidine.*

$$\begin{array}{l}NH\cdot CH \\ | \\ CH{=}N\end{array}\!\!>\!C\cdot CH_2\cdot CH(NH_2)\cdot CO_2H.$$

Two and a-half grams of *r*-α-chloro-β-glyoxaline-4(or 5)-propionic acid were dissolved in 50 c.c. of concentrated ammonia (D 0·880), and heated at 110° under pressure for three hours. The liquor was then evaporated to dryness under diminished pressure, and the residue dissolved in a little water and again evaporated. The residue was dissolved in a few c.c. of water, and set aside, when 1·1 grams of r-*histidine monohydrochloride* separated in stout needles, melting at 110—115°; after recrystallisation from water, this salt melted at 117—119° (corr.), after sintering earlier.

A larger quantity of synthetic *r*-histidine was then prepared as follows: Twenty grams of ethyl 4(or 5)-glyoxalinemethylchloromalonate were converted into *r*-α-chloro-β-glyoxaline-4(or 5)-propionic acid hydrochloride by boiling for half an hour with 200 c.c. of 20 per cent. hydrochloric acid, and evaporating the liquor to dryness under diminished pressure.

The resulting colourless varnish was again twice dissolved in water, and evaporated to dryness to remove free hydrochloric acid. It was then dissolved in 240 c.c. of concentrated ammonia (D 0·880), and heated under pressure to 110° for three hours. The liquor was then evaporated to dryness under diminished pressure to remove the excess of ammonia, and the residue dissolved in about 40 c.c. of water. On keeping overnight in an evacuated desiccator over sulphuric acid, the liquor was covered with a crust of ammonium chloride. After the removal of this by filtration, the filtrate began to deposit crystals, and on keeping became semi-solid. The crystals were collected after about half an hour, and, after recrystallisation from water, melted at 117—119° (corr.); they were r-*histidine monohydrochloride.* On concentrating the mother liquors, further crops of this salt and ammonium chloride were obtained; these were separated by fractional crystallisation from water, and a total quantity of 6·3 grams of *r*-histidine monohydrochloride was isolated in a pure state; this yield is 38 per cent. of the theoretical.

Synthetic r-*Histidine.*

r-*Histidine monohydrochloride* forms clusters of stout needles (from water), which sinter at 112°, and melt at 117—119° (corr.). It contains two molecules of water of crystallisation, of which only about 1½ molecules are lost at 100°. This salt is easily soluble in water, but sparingly so in alcohol:

0·1556 * lost 0·0196 at 100°. $H_2O=12·6$.
0·1530 * gave 0·1781 CO_2 and 0·0857 H_2O. C=31·7; H=6·3.
0·1009 * „ 16·0 c.c. N_2 at 16° and 765 mm. N=18·9.
0·1634 * „ 0·1010 AgCl. Cl=15·3.
$C_6H_9O_2N_3,HCl,2H_2O$ requires C=31·6; H=6·2; N=18·5; Cl=15·6; and $1\frac{1}{2}H_2O=11·9$ per cent.

When this salt was dissolved in a little water, and a large excess of absolute alcoholic hydrogen chloride added, the dihydrochloride was precipitated in an amorphous form, but quickly became a crystalline powder on stirring. This salt began to sinter at 230°, and decomposed at 235—236° (corr.):

0·1505 gave 0·1750 CO_2 and 0·0638 H_2O. C=31·7; H=4·8.
0·1088 „ 0·1359 AgCl. Cl=30·9.
$C_6H_9O_2N_3,2HCl$ requires C=31·6; H=4·9; Cl=31·1 per cent.

On dissolving the dihydrochloride in a little water and adding alcohol, the sesquihydrochloride separated on keeping in clusters of prismatic needles, which melted at 168—170° (corr.).

These three hydrochlorides of synthetic *r*-histidine were compared with the corresponding salts of *r*-histidine prepared by racemising *l*-histidine, and found to be identical with them; in each case the corresponding salt and the mixture of the synthetic and racemised salt melted simultaneously.

The melting point of racemised histidine dihydrochloride, given by Fränkel (*loc. cit.*) as 220°, and by Ewins and Pyman (*loc. cit.*) as 225° (corr.), is too low; a re-determination has shown that it should be 235—236° (corr.).

r-*Histidine* was prepared from the synthetic monohydrochloride by digesting it with silver oxide, and filtering to remove silver chloride, removing the excess of silver with hydrogen sulphide, and evaporating to low bulk under diminished pressure. After recrystallisation from water, it formed well defined quadrilateral plates, which decomposed at 283° (corr.) simultaneously with a specimen prepared by racemising *l*-histidine, and a mixture of the two in the same bath. It is anhydrous, and is sparingly soluble in cold water, easily so in hot water, but almost insoluble in absolute alcohol and the other usual organic solvents:

0·1514 gave 0·2551 CO_2 and 0·0806 H_2O. C=46·0; H=6·0.
0·0859 „ 20·0 c.c. N_2 at 22° and 763 mm. N=27·0.
$C_6H_9O_2N_3$ requires C=46·4; H=5·9; N=27·1 per cent.

r-Histidine dipicrate was also prepared from the synthetic monohydrochloride, and proved to be identical with the salt described by Ewins and Pyman (*loc. cit.*). It should be mentioned that this

* Air-dried.

salt—from either source—when dried in the air for only a short time, melts at about 103° (corr.), and then, after drying at 100°, sometimes melts between 140° and 150°, although it does not decompose until 190°. When thoroughly air-dried, however, and then dried at 100°, it sinters at about 183°, and melts and decomposes at 190° (corr.).

Resolution of r-*Histidine.*

With the object of finding a suitable method for the resolution of synthetic *r*-histidine, some salts of natural histidine with optically active acids were first prepared.

The histidine used for this purpose was prepared from hæmoglobin, and the free base was obtained from its hydrochloride by means of silver carbonate, a method due to Fränkel (*Monatsh.*, 1903, **24**, 229). The base decomposed at 287° (corr.), a temperature considerably higher than that given by Fränkel, namely 253°, and it was therefore analysed. (Found, C=46·0; H=6·1. Calc., C=46·4; H=5·9 per cent.)

Its specific rotatory power was then determined in a 1-dcm. tube:

0·2, in 10 c.c. of water at 26°, gave α_D −0·74°, whence $[\alpha]_D$ −37·0°.

1·015, in 25 c.c. of water at 28°, gave α_D −1·49°, whence $[\alpha]_D$ −36·7°.

Kossel and Kutscher (*Zeitsch. physiol. Chem.*, 1899, **28**, 382) give $[\alpha]_D$ −39·7°.

It was found that the *d*-camphorsulphonate and neutral *d*-tartrate of this base were very readily soluble in water, and crystallised from this solvent with difficulty.

l-*Histidine* d-*hydrogen tartrate*, however, crystallises from water in beautiful, large, clear, colourless, well defined prisms, often separating in triangular plates with bevelled edges. It is anhydrous, and easily soluble in water. This salt decomposes at 172—173° (corr.):

0·1535 gave 0·2188 CO_2 and 0·0718 H_2O. C=38·9; H=5·2.

$C_6H_9O_2N_3,C_4H_6O_6$ requires C=39·3; H=5·0 per cent.

The specific rotatory power of this salt was determined in a 2-dcm. tube; it appears to diminish with increasing concentration:

0·1616, in 15 c.c. of water at 24°, gave α_D +0·37°, whence $[\alpha]_D$ +17·2.

0·5587, in 15 c.c. of water at 24°, gave α_D +1·26°, whence $[\alpha]_D$ +16·9.

0·7474, in 15 c.c. of water at 25°, gave α_D +1·62°, whence $[\alpha]_D$ +16·3.

The base was then regenerated from the pure salt as follows, the

method adopted being substantially that used by Fränkel (*loc. cit.*) for the isolation of histidine from the hydrolytic products of hæmoglobin. The tartrate was dissolved in a large volume of water, and precipitated by mercuric chloride and sodium carbonate; the precipitate was thoroughly washed with water, dissolved in dilute hydrochloric acid, and treated with hydrogen sulphide. After the removal of mercuric sulphide, the liquor was evaporated to dryness under diminished pressure, moistened with water, and again evaporated to dryness to remove free hydrochloric acid. The residue was then dissolved in water, shaken with silver carbonate, filtered from silver chloride, treated with hydrogen sulphide, filtered from silver sulphide, and evaporated to low bulk, when the base crystallised out.

Its specific rotatory power was determined in a 2-dcm. tube:

0·504, in 15 c.c. of water at 22°, gave $\alpha_D -2{\cdot}53°$, whence $[\alpha]_D -37{\cdot}7°$.

In view of the satisfactory crystalline nature of *l*-histidine *d*-hydrogen tartrate, it was determined to attempt the resolution of synthetic *r*-histidine by fractional crystallisation of the *d*-hydrogen tartrate, and 0·73 gram of synthetic *r*-histidine and 0·7 gram of *d*-tartaric acid were accordingly dissolved in a little water and kept. After a short time there crystallised out 0·6 gram of a sparingly soluble salt, melting at 234° (corr.), which is subsequently shown to be *d*-histidine *d*-hydrogen tartrate, and the mother liquors from this salt, after spontaneous evaporation in a desiccator over sulphuric acid, deposited about 0·2 gram of clear prisms, melting at 172—173° (corr.), which were identical with *l*-histidine *d*-hydrogen tartrate. The resolution of a larger quantity of synthetic histidine was then carried out as follows: 3·5 grams of synthetic *r*-histidine and 3·4 grams of *d*-tartaric acid were dissolved in water, and evaporated to a volume of about 20 c.c., when crystals began to separate from the hot solution. The evaporation was then continued to a volume of about 15 c.c., and the liquor set aside. Clusters of prisms, melting at 234° (corr.), and amounting to 2·9 grams, were then collected, and on concentrating the mother liquor and keeping, a further 0·28 gram of the same salt were obtained.

On recrystallising this salt from water, 3·05 grams of *d*-histidine *d*-hydrogen tartrate were obtained.

d-*Histidine* d-*hydrogen tartrate* crystallises from water in clusters of small prisms, which decompose at 234° (corr.). It dissolves in 25 to 30 parts of cold water, and more readily in hot water. It is anhydrous:

0·1561 gave 0·2237 CO_2 and 0·0694 H_2O. C=39·1; H=5·0.
$C_6H_9O_2N_3,C_4H_6O_6$ requires C=39·3; H=5·0 per cent.

Its specific rotatory power was determined in a 2-dcm. tube:

0·9220, in 25 c.c. of water at 28°, gave α_D +0·98°, whence $[\alpha]_D$ +13·3°.

This salt was converted into the free base by the method given above.

d-*Histidine* crystallises from water in beautiful, colourless, monoclinic plates, forming elongated hexagons. It decomposes at 287—288° (corr.), and is anhydrous. It is sparingly soluble in cold water, easily so in hot water, and almost insoluble in absolute alcohol and the other usual organic solvents:

0·1532 gave 0·2608 CO_2 and 0·0807 H_2O. C=46·4; H=5·9.
$C_6H_9O_2N_3$ requires C=46·4; H=5·9 per cent.

Its specific rotatory power was determined in a 2-dcm. tube:

0·401, in 15 c.c. of water at 23°, gave α_D +2·10°, whence $[\alpha]_D$ +39·3°.

The mother liquor from the *d*-histidine *d*-hydrogen tartrate was then somewhat concentrated, and inoculated with a trace of the *l*-histidine *d*-hydrogen tartrate obtained in the preliminary experiment mentioned above, when there crystallised 1·65 grams of this salt in clear prisms, decomposing at 172—173° (corr.), and on concentrating the mother liquors, a further 1·05 grams, equally pure. The ultimate mother liquors which continued to deposit crystalline material were neglected.

The melting point of the *l*-base-*d*-acid was unchanged by recrystallising the salt, or mixing it with natural *l*-histidine *d*-hydrogen tartrate. The salt was, however, recrystallised, and its specific rotatory power was determined in a 2-dcm. tube, and found to be in agreement with that of the natural salt at corresponding concentrations:

0·8625, in 25 c.c. of water at 27°, gave α_D +1·20°, whence $[\alpha]_D$ +17·4°.

0·8200, in 15 c.c. of water at 23°, gave α_D +1·76°, whence $[\alpha]_D$ +16·1°.

The recrystallised salt and its mother liquor (=2·7 grams of *l*-base-*d*-acid) were then recombined, and the base regenerated.

The specific rotatory power of the latter was determined in a 2-dcm. tube:

0·4143, in 15 c.c. of water at 26°, gave α_D −2·02°, whence $[\alpha]_D$ −36·6°.

This figure being somewhat low, the whole of the regenerated

base (1·1 grams) was converted into the *l*-hydrogen tartrate, and crystallised from water.

l-*Histidine* l-*hydrogen tartrate* crystallises from water in clusters of prisms, which decompose at 234° (corr.). It is sparingly soluble in cold water. A specimen of this salt prepared from natural histidine had the same melting point and specific rotatory power. The latter was determined in a 2-dcm. tube:

0·6792 (synthetic), in 15 c.c. of water at 22°, gave α_D −1·10°, whence $[\alpha]_D$ −12·1°.

0·6796 (natural), in 15 c.c. of water at 25°, gave α_D −1·10°, whence $[\alpha]_D$ −12·1°.

The synthetic salt was then converted into the free base in the usual way.

Synthetic *l*-histidine crystallised from water in monoclinic plates, forming elongated hexagons, which decomposed at 287—288° (corr.). Its decomposition point is not depressed by admixture of the base with natural *l*-histidine, but this is of little importance, since it is only depressed about 2° by admixture with *r*-histidine. It is sparingly soluble in cold water, easily so in hot water, and almost insoluble in absolute alcohol and the other usual organic solvents:

0·1402 gave 0·2358 CO_2 and 0·0756 H_2O. C=45·9; H=6·0.

$C_6H_9O_2N_3$ requires C=46·4; H=5·9 per cent.

Its specific rotatory power was determined in a 2-dcm. tube:

0·3447, in 15 c.c. of water at 26°, gave α_D −1·75°, whence $[\alpha]_D$ −38·1°.

r-α-*Hydroxy*-β-*glyoxaline*-4(or 5)-*propionic Acid*,

$$\begin{array}{l} NH{\cdot}CH \\ |\\ CH{=}N \end{array}\!\!>\!C{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H.$$

This acid results from the action of silver hydroxide on a hot aqueous solution of *r*-α-chloro-β-glyoxaline-4(or 5)-propionic acid. After the removal of silver chloride, the solution is treated with hydrogen sulphide, filtered from silver sulphide, and concentrated, when the hydroxy-acid crystallises out.

r-α-*Hydroxy*-β-*glyoxaline*-4(or 5)-*propionic acid* crystallises from water in prisms, which, after drying at 100°, melt at 222° (corr.). It contains one molecule of water of crystallisation, which is not lost at 100°, and is sparingly soluble in cold water or alcohol, but readily so in hot water:

0·1516 * gave 0·2290 CO_2 and 0·0776 H_2O. C = 41·2; H = 5·7.
0·1007 * ,, 14·0 c.c. N_2 at 16° and 755 mm. N = 16·3.
$C_6H_8O_3N_2,H_2O$ requires C = 41·4; H = 5·8; N = 16·1 per cent.

Oxydeaminohistidine, the α-hydroxy-β-glyoxaline-4(or 5)-propionic acid obtained by the action of silver nitrite on *l*-histidine hydrochloride, also crystallises with $1H_2O$. It melts at 204° (Fränkel, *Monatsh.*, 1903, **24**, 229), and is, of course, the optically active variety corresponding with *l*-histidine.

4(or 5)-*Glyoxalinemethylchloromalonamide*,
$C_3H_3N_2 \cdot CH_2 \cdot CCl(CO \cdot NH_2)_2$.

One gram of ethyl 4(or 5)-glyoxalinemethylchloromalonate hydrochloride was dissolved in a mixture of 20 c.c. of concentrated ammonia and 10 c.c. of alcohol, and the clear solution kept overnight. It was then evaporated to dryness under diminished pressure, the residue extracted with absolute alcohol, and filtered to remove ammonium chloride, these operations being repeated two or three times. The final alcoholic residue occurred as a varnish, which gave, with absolute alcoholic hydrogen chloride, 0·7 gram of 4(or 5)-*glyoxalinemethylchloromalonamide hydrochloride* as a crystalline precipitate. This salt was dissolved in a little water and mixed with absolute alcoholic hydrogen chloride, and on keeping separated in very pale buff, long, clear spikes, which darkened at 240° and decomposed at 245° (corr.).

It is anhydrous, readily soluble in water, but sparingly so in alcohol:

0·1500 gave 0·1821 CO_2 and 0·0567 H_2O. C = 33·1; H = 4·2.
0·0805 ,, 14·8 c.c. N_2 at 18° and 766 mm. N = 21·7.
0·1858 ,, 0·2100 AgCl. Cl = 27·9.
$C_7H_9O_2N_4Cl,HCl$ requires C = 33·2; H = 4·0; N = 22·1; Cl = 28·0 per cent.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

* Dried at 100°.

CLVIII.—*The Interaction of Metallic Oxides and Phosphoryl Chloride, Alone and in the Presence of Certain Organic Compounds.*

By HENRY BASSETT, jun., and HUGH STOTT TAYLOR.

APATITE, $(Ca_3P_2O_8)_3,CaF_2$, and wagnerite, $Mg_3P_2O_8,MgF_2$, are two important minerals, the formulæ of which are usually written as indicated, suggesting that the compounds are to be regarded as complex derivatives of the metallic fluoride (or, in some cases, chloride), in which the halogen is directly attached to the metal.

There is, however, little experimental foundation for such an assumption, and in some ways it is perhaps more probable that the halogen is more closely associated with the phosphorus.

The following investigation was commenced in the hope that by preparing simple chlorophosphates and determining their constitution, it would be possible to throw light on the nature of more complex halogen compounds such as the above.

We found that when freshly ignited lime and freshly distilled phosphoryl chloride were mixed and allowed to remain at the ordinary temperature or gently boiled, a well crystallised compound was gradually formed, which analysis showed to have the formula $CaO,2POCl_3$.

This behaviour is not restricted to lime, and magnesia gives either $MgO,2POCl_3$ or $MgO,3POCl_3$, according to the conditions of the experiment. We have also obtained well crystallised compounds, $MnO,3POCl_3$ and $ZnO,3POCl_3$, but not in an absolutely pure state, owing to various difficulties which will be referred to shortly. Lime also yields a compound with three molecules of phosphoryl chloride in certain circumstances.

All the other metallic oxides which we have investigated (CdO, CoO, CuO, Cu_2O, HgO, Al_2O_3, Fe_2O_3) react with phosphoryl chloride, but apparently not in such a simple manner as do lime and magnesia, and the chloride of the metal appears to be the chief product.

As was to be expected, these compounds of phosphoryl chloride are extremely sensitive to moisture, and in consequence of this the analyses often show low values for the chlorine, and a deficit, sometimes of several per cent., which it is almost impossible to prevent entirely.

In such cases, if the deficit is taken to be due to the replacement of a certain amount of chlorine by hydroxyl, it is found that the

atomic ratio of the total chlorine to phosphorus is almost exactly as three to one, as it should be, of course, for a compound of phosphoryl chloride.

Having found that phosphoryl chloride and certain oxides readily combined to give the compounds above mentioned, the effect of solvents on the course of the reaction was investigated.

It was found that when lime was added to a solution of phosphoryl chloride in acetone, ethyl acetate, methyl benzoate, or ethyl benzoate, which had been dried over calcium chloride and redistilled, a vigorous reaction occurred, which in the first two cases was sufficient to cause the solvent to boil. Some hydrogen chloride is evolved during this process, and the lime passes into solution. The solution on cooling deposits beautiful prismatic crystals, the analyses of which correspond very closely with the formulæ:

$CaO,P_2O_3Cl_4,2C_3H_6O$; $CaO,P_2O_3Cl_4,2C_4H_8O_2$; $CaOP_2O_3Cl_4,2C_8H_8O_2$; and $CaO,P_2O_3Cl_4,2C_9H_{10}O_2$.

These compounds are clearly the compound $CaO,P_2O_3Cl_4$ crystallised with two molecules of ketone or ester. In agreement with this view is the fact that the organic part of the molecule can be changed by simple recrystallisation from another solvent. Thus by recrystallising the ethyl acetate compound from acetone, the acetone compound is obtained and vice versa.

Exactly similar organic derivatives have been obtained, using magnesium oxide and manganous oxide.

The formation of these organic compounds is brought about by traces of moisture present in the organic solvents, or which are absorbed during the course of the experiment, and there is some reason for thinking that the moisture acts preferably on the previously formed compound $CaO,2POCl_3$, rather than on the phosphoryl chloride. In any case, the organic compounds can be obtained equally well by treating the previously prepared compound $CaO,2POCl_3$ with the organic solvent in which it dissolves, yielding a solution from which the organic derivative of the compound $CaO,P_2O_3Cl_4$ crystallises.

The compounds of pyrophosphoryl chloride, $P_2O_3Cl_4$, obtained by us seem of especial interest as confirming the results obtained by Besson (*Compt. rend.*, 1897, **124**, 1099), who showed that this compound is the first product of the action of moisture on phosphoryl chloride which can be isolated. He was, however, never able to obtain more than a very small amount of pyrophosphoryl chloride in this way. It is therefore of interest to obtain derivatives of this compound which indicate quantitative conversion of phosphoryl chloride into pyrophosphoryl chloride, derivatives, moreover, which are well crystallised and well defined. On solution of these

in water, orthophosphoric acid is formed immediately, and this is in agreement with the behaviour of pyrophosphoryl chloride itself, as stated by Geuther and Michaelis (*Ber.*, 1871, **4**, 766).

No compounds of phosphoryl chloride with oxides have been obtained by previous workers, and from what has been said it will be seen that the statement found sometimes (Dammer "Handbuch," 1894, II., **1**, 134; Casselmann, *Annalen*, 1856, **98**, 228) that phosphoryl chloride reacts with metallic oxides to form chloride and phosphate of the metal requires qualifying. Gustavson (*J. Russ. Phys. Chem. Soc.*, 1871, **3**, 225) showed that boron trioxide and phosphoryl chloride react with formation of a double compound, $BCl_3,POCl_3$.

The oxidic compounds described in the present paper seem of especial interest from the fact that any salt-like character is only very feebly developed, their behaviour being more typical of that of "molecular compounds." This is unusual in the case of metallic oxides which usually give rise to salts. We consider, however, that there is no fundamental structural difference between, for example, $CaO,2POCl_3$ and $CaO,2PO(OH)_3$ [$CaH_4P_2O_8,H_2O$], and that from some points of view the first compound may be regarded as derived from the second by replacement of the hydroxyl groups by chlorine. It seems to us also that the existence of such compounds as $CaO,2POCl_3$ lends some support to the view that even in compounds like apatite and wagnerite the halogen is directly attached to phosphorus. We are seeking further evidence in favour of this view.

We hope to discuss the precise nature of the compounds of phosphoryl chloride and pyrophosphoryl chloride in another paper, as well as the mechanism of the reaction between phosphoryl chloride and metallic oxide which leads to the formation of metallic chloride in certain cases.

Experimental.

Reactions between Oxides and Phosphoryl Chloride.

In the following experiments the freshly ignited oxide was added to excess of freshly distilled phosphoryl chloride. The mixture enclosed in a sealed tube was, except when otherwise stated, heated to 110° in an oil-bath until examination showed that the oxide had reacted completely. The crystalline solid was then collected, and drained on porous plate in a desiccator containing potassium hydroxide and sulphuric acid until dry and powdery. In all these operations precautions were taken to exclude moisture as far as possible.

$CaO,2POCl_3$.—The quantities of lime and phosphoryl chloride

employed averaged about 0·56 gram and 10 c.c. respectively. The lime was gradually converted into a crystalline powder consisting of small, rectangular prisms. The length of time required for this transformation varied considerably, but was never less than two days at 110°. The following analyses refer to different preparations:

Found: CaO = 16·16, 16·22, 15·15; P_2O_5 = 38·62, 39·33, 39·92; Cl = 58·58, 56·16, 57·89.

$CaO,2POCl_3$ requires CaO = 15·43; P_2O_5 = 39·1; Cl = 58·64 per cent.

From the appearance of the crystals formed, it is clear that the compound $CaO,2POCl_3$ is also formed when lime and phosphoryl chloride interact at 25° or at the room temperature, but the change taking place very slowly under these conditions has not time for completion before a further change sets in. This causes the contents of the tube to become pasty, owing to the formation of a very fine solid. We have not been able to obtain satisfactory analyses of this solid owing to the difficulty of separating it from the excess of phosphoryl chloride, but those we have made point to the formation of a compound $CaO,3POCl_3$.

The compound $CaO,2POCl_3$ is exceedingly sensitive to moisture, and dissolves at once in water, yielding a strongly acid solution.

$MgO,2POCl_3$ *and* $MgO,3POCl_3$.—Magnesium oxide reacts far more readily with phosphoryl chloride than does lime, which is probably chiefly due to the fact that the magnesium compound is markedly soluble in phosphoryl chloride, whereas the calcium compound is insoluble.

On heating magnesium oxide and phosphoryl chloride in a sealed tube to 110°, one of two things may happen: either the oxide is slowly converted into a crystalline compound without any marked evidence of solution, or else practically all the oxide may dissolve. The solution obtained in the latter case deposits large (5 mm.) and well defined crystals on cooling, although it may remain supersaturated for a considerable time.

The compound obtained in the first case consists of $MgO,2POCl_3$, and in the second case of $MgO,3POCl_3$.

Which course the reaction takes seems to be more or less a matter of accident:

Found: MgO = 11·14; P_2O_5 = 42·38; Cl = 62·95.

$MgO,2POCl_3$ requires MgO = 11·60; P_2O_5 = 40·88; Cl = 61·33 per cent.

Found: MgO = 7·8; P_2O_5 = 43·2; Cl = 63·2.

$MgO,3POCl_3$ requires MgO = 8·07; P_2O_5 = 42·52; Cl = 63·79 per cent.

The phosphoryl chloride in these compounds is relatively loosely held. It can be slowly removed by simply washing with light petroleum or by the action of heat. Then again the chemical behaviour of the compounds described is very similar to that of phosphoryl chloride itself. Thus, when the compound $CaO,2POCl_3$ is treated with moist air or alcohol, all the chlorine is removed as hydrogen chloride; whilst one molecule of $CaO,2POCl_3$ reacts with 8 molecules of aniline or 12 molecules of ammonia just as two molecules of phosphoryl chloride would.

From this behaviour it is to be concluded that the compounds described in this paper belong to that large group of compounds called, somewhat vaguely, "molecular compounds."

$MnO,3POCl_3$.—Manganous oxide is slowly converted into a very pale pink substance when heated to 110° with phosphoryl chloride. This seems to consist chiefly of manganous chloride with a considerable amount of the compound $MnO,3POCl_3$. The latter is sparingly soluble in phosphoryl chloride, which renders its separation from the manganous chloride possible. The mixture of manganous oxide and phosphoryl chloride is sealed up in a fairly long, stout tube bent at an angle of about 90°. The materials are heated in one limb to 110° until the liquid is saturated, when it is carefully decanted into the other limb, where, on cooling, crystals of the compound $MnO,3POCl_3$ are deposited. The liquid is then poured back into the other limb and again saturated, and these processes continued until sufficient crystals have accumulated. The tube is then opened, and the solid products separated for analysis. It is not easy to obtain more than a small quantity of the compound in this way, and owing to the smallness of the crystals the difficulty of separating and handling it is intensified. The result is that a considerable amount of moisture is almost inevitably absorbed, so that the analyses are not very satisfactory:

Found: $MnO = 13{\cdot}14$; $P_2O_5 = 41{\cdot}3$; $Cl = 53{\cdot}52$.

$MnO,3POCl_3$ requires $MnO = 13{\cdot}35$; $P_2O_5 = 40{\cdot}08$; $Cl = 60{\cdot}12$ per cent.

After allowing for the oxygen-equivalent of the chlorine there is a deficit of 4·44 per cent. due to moisture absorbed during the handling and in the desiccator, this moisture being partly present as such, and having partly reacted with the chlorine to evolve hydrogen chloride.

During one experiment the formation of large, pink crystals was observed at one stage. These were not, however, separated, and could not be obtained again. They very possibly consisted of the compound $MnO,2POCl_3$, for we have obtained a beautiful ethyl

acetate derivative of this compound, $MnO,P_2O_3Cl_4,2C_4H_8O_2$, which will be described presently.

Action of Phosphoryl Chloride on Zinc Oxide.—Large amounts of zinc oxide will dissolve in phosphoryl chloride at the ordinary temperature with considerable ease. If the phosphoryl chloride be in moderate excess, about ten days are required for complete solution; the less the excess of phosphoryl chloride the longer is the time required, and the more viscous is the resulting clear solution. When the reagents were mixed in the proportion of one molecule of zinc oxide to two of phosphoryl chloride, and the tube left on its side so as to bring a large surface of the oxide in contact with the liquid, a homogeneous solution which was so viscous as almost to constitute a glass was obtained after six months.

A mixture in the proportion of one molecule of zinc oxide to three of phosphoryl chloride had, after three months, deposited crystals consisting chiefly of small, rhombic plates, possibly mixed with some of another kind. The solution, originally viscous, was now quite mobile.

Analysis of the crystals gave:

Found: $ZnO = 22{\cdot}40$; $P_2O_5 = 32{\cdot}86$; $Cl = 56{\cdot}81$.

Allowing for the oxygen equivalent of the chlorine, we have $112{\cdot}07 - 12{\cdot}80 = 99{\cdot}27$, showing a deficit (moisture) of 0·73 per cent.

This corresponds very closely with a mixture of 76·93 per cent. of the compound $ZnO,3POCl_3$ and 23·07 per cent. of zinc chloride.

The action of heat on the clear solutions of zinc oxide in phosphoryl chloride is somewhat peculiar. On raising the temperature they become turbid, and gradually separate into two liquid layers, the lower of which is more viscous than the other. The temperature at which this separation begins depends on the concentration of the zinc oxide. The greater the concentration the lower is the temperature required. If too little zinc oxide is present, no separation may occur, even at 100°. With one gram of zinc oxide in about 15 grams of phosphoryl chloride, separation into two layers began at 56°. On gradually raising the temperature, while more and more of the lower viscous layer separated, it at the same time gave off bubbles of the more mobile liquid, and became in consequence still more viscous. The mutual solubility of the two liquids clearly diminishes with rise of temperature; on cooling, the two again mix completely.

An experiment was performed in which a solution of zinc oxide in phosphoryl chloride was heated to 100° in a wide tube sealed at one end to a narrow one. The tube was held vertically, so that the viscous liquid collected in the narrow part. When separation

was complete, the tube was removed from the bath, and inverted to separate the mobile from the viscous liquid. The latter on cooling became almost a glass, and the portion of the tube containing it was cut off. It was weighed, and the contents analysed:

Found: $ZnO = 21{\cdot}24$; $P_2O_5 = 36{\cdot}45$; $Cl = 54{\cdot}61$.
$ZnO,2POCl_3$ requires $ZnO = 20{\cdot}96$; $P_2O_5 = 36{\cdot}60$; $Cl = 54{\cdot}81$ per cent.

It is doubtful whether such a product can be regarded as a definite compound.

Action of Phosphoryl Chloride on Other Oxides.—Cadmium, cobaltous, cupric, cuprous, mercuric, ferric, and aluminium oxides all react with phosphoryl chloride, both at the ordinary temperature and when heated to 100°, but the rate of reaction is in most cases slow, and varies considerably. In all cases the colour of the product formed is that of the anhydrous chloride, of which it seems chiefly composed. We have only actually separated and analysed the solid in the case of cadmium and cupric oxides. In the case of ferric oxide a large amount dissolves in the phosphoryl chloride, which becomes dark reddish-brown.

Owing to the difficulty of separation, the analysis of the cadmium product was not satisfactory, but was sufficient to show that one was dealing with a mixture containing a large percentage of cadmium chloride.

The product obtained from cupric oxide could be more easily handled, and two experiments gave the following analytical results:

Found: $CuO = 46{\cdot}96, 55{\cdot}51$; $P_2O_5 = 14{\cdot}31, 16{\cdot}36$; $Cl = 46{\cdot}54, 37{\cdot}51$.

The second experiment was carried out in a sealed tube, and several weeks were required for all the oxide to react. The analysis corresponds closely with a mixture of 25·48 per cent. of copper metaphosphate * and 74·52 per cent. of cupric chloride, although there is slightly too much copper, probably present as unaltered oxide.

In the first experiment, which was carried out in a flask fitted with ground-in air condenser and calcium chloride drying tube, the reaction only required twenty-four hours, but the analysis shows a deficit of 2·77 per cent. If this is regarded as moisture which has replaced chlorine by hydroxyl, the analytical figures would indicate a mixture of 38·97 per cent. of the compound $CuO,2POCl_3$ and 61·03 per cent. of cupric chloride.

Compounds of the Type $MO,P_2O_3Cl_4,2X$ (where X = the organic

* On treating the product with water a slate-coloured solid (probably the metaphosphate) separated, which only dissolved slowly after the addition of nitric acid.

solvent).—These were all obtained by adding the freshly ignited oxide to a solution of phosphoryl chloride in the organic liquid, which had been dried over calcium chloride and freshly distilled. It is best to only use a little more than two molecules of phosphoryl chloride to one of oxide. Solution was assisted when necessary by gentle heating, the mixture being contained in a flask with ground-in air condenser closed by a calcium chloride tube. The solution was then allowed to crystallise in a desiccator containing solid potassium hydroxide and concentrated sulphuric acid. The crystals separating were washed with a small quantity of the solvent, drained on porous plate in the desiccator, and analysed. Under these conditions sufficient moisture was present in the solvent or absorbed during the experiment to effect the displacement of the two atoms of chlorine. The hydrogen chloride thus formed can be absorbed and estimated, as was actually done in one or two cases. On solution in water these compounds are completely decomposed with separation of the organic portion of the molecule—which in a few cases was directly estimated. As a rule, however, it was obtained by difference.

$CaO,P_2O_3Cl_4,2(CH_3{\cdot}CO{\cdot}CH_3)$.—This forms beautiful transparent crystals several mm. long, which are sparingly soluble in cold acetone. During the preparation of this compound the solution becomes brown owing to the condensing action of the liberated hydrogen chloride on the acetone. By carefully washing the crystals they can be obtained colourless, and then keep fairly well in a sealed tube. If not properly washed they soon become brown:

Found: $CaO = 13{\cdot}73, 13{\cdot}48$; $P_2O_5 = 33{\cdot}23, 34{\cdot}20$; $Cl = 33{\cdot}13, 34{\cdot}08$; C_3H_6O (by diff.) $= 27{\cdot}37, 25{\cdot}92$.

$CaO,P_2O_3Cl_4,2C_3H_6O$ requires $CaO = 13{\cdot}21$; $P_2O_5 = 33{\cdot}49$; $Cl = 33{\cdot}45$; $C_3H_6O = 27{\cdot}39$ per cent.

In the second experiment the crystals had been left for forty-eight hours in an evacuated desiccator containing sulphuric acid, and had evidently lost a little acetone.

$MnO,P_2O_3Cl_4,2(CH_3{\cdot}CO{\cdot}CH_3)$.—In this case a considerable amount of manganous chloride is formed, from which the acetone solution must be decanted. On crystallisation, small prisms of a pale pink colour are obtained. The analysis is not very satisfactory, probably owing to the presence of a certain amount of manganous chloride:

Found: $MnO = 16{\cdot}44$; $P_2O_5 = 31{\cdot}66$; $Cl = 33{\cdot}14$; C_3H_6O (by diff.) $= 26{\cdot}24$.

$MnO,P_2O_3Cl_4,2C_3H_6O$ requires $MnO = 16{\cdot}78$; $P_2O_5 = 33{\cdot}59$; $Cl = 33{\cdot}55$; $C_3H_6O = 23{\cdot}65$ per cent.

$CaO,P_2O_3Cl_4,2(C_2H_5{\cdot}O{\cdot}CO{\cdot}CH_3)$. — This compound crystallises readily in long prisms, only sparingly soluble in cold ethyl acetate:

Found: $CaO = 11{\cdot}69$; $P_2O_5 = 29{\cdot}57$; $Cl = 29{\cdot}14$; $C_4H_8O_2$ (by diff.) $= 36{\cdot}27$.

$CaO,P_2O_3Cl_4,2C_4H_8O_2$ requires $CaO = 11{\cdot}57$; $P_2O_5 = 29{\cdot}34$; $Cl = 29{\cdot}31$; $C_4H_8O_2 = 36{\cdot}39$ per cent.

$MgO,P_2O_3Cl_4,2(C_2H_5{\cdot}O{\cdot}CO{\cdot}CH_3)$.—This was prepared in just the same way as the calcium compound. The ethyl acetate solution has, however, a marked tendency to remain supersaturated. Fine crystals can be obtained, very similar to, but larger than, those of the calcium compound. The prisms are fairly broad, and may be from 0·5 to 1·0 cm. long:

Found: $MgO = 8{\cdot}55, 8{\cdot}56$; $P_2O_5 = 30{\cdot}57, 28{\cdot}84$; $Cl = 30{\cdot}70, 30{\cdot}48$; $C_4H_8O_2$ (by diff.) $= 37{\cdot}10, 39{\cdot}00$.

$MgO,P_2O_3Cl_4,2C_4H_8O_2$ requires $MgO = 8{\cdot}74$; $P_2O_5 = 30{\cdot}32$; $Cl = 30{\cdot}28$; $C_4H_8O_2 = 37{\cdot}59$ per cent.

The second analysis refers to a preparation obtained from the action of ethyl acetate on previously prepared $MgO,3POCl_3$.

$MnO,P_2O_3Cl_4,2(C_2H_5{\cdot}O{\cdot}CO{\cdot}CH_3)$.—A small quantity of manganous chloride is commonly formed in this preparation, from which the solution is decanted into the crystallising dish. The compound forms magnificent pink prisms, somewhat resembling cubes, and several mm. long:

Found: $MnO = 14{\cdot}25$; $P_2O_5 = 28{\cdot}34$; $Cl = 28{\cdot}76$; $C_4H_8O_2$ (by diff.) $= 35{\cdot}11$.

$MnO,P_2O_3Cl_4,2C_4H_8O_2$ requires $MnO = 14{\cdot}22$; $P_2O_5 = 28{\cdot}48$; $Cl = 28{\cdot}44$; $C_4H_8O_2 = 35{\cdot}27$ per cent.

This compound is clearly derived from the compound $MnO,2POCl_3$, although we have not actually obtained that compound itself.

$CaO,P_2O_3Cl_4,2(C_2H_5{\cdot}O{\cdot}CO{\cdot}C_6H_5)$.—This is a white compound, crystallising in small prisms, moderately soluble in hot ethyl benzoate. On solution of the solid in water, the ester, being insoluble, separates out. It was collected, dissolved in ether, the ethereal solution washed and dried, the ether driven off, and the residual ester weighed:

Found: $CaO = 8{\cdot}50$; $P_2O_5 = 22{\cdot}21$; $Cl = 20{\cdot}88$; $C_9H_{10}O_2 = 50{\cdot}0$ (by diff. $= 55{\cdot}46$).

$CaO,P_2O_3Cl_4,2C_9H_{10}O_2$ requires $CaO = 9{\cdot}21$; $P_2O_5 = 23{\cdot}35$; $Cl = 23{\cdot}32$; $C_9H_{10}O_2 = 49{\cdot}34$ per cent.

The solid analysed contained a small quantity of adhering ester, which it is impossible to remove completely on porous plate. On this account, in the following preparation of the methyl derivative

the free ester was removed by distillation at 100° in a Töpler vacuum.

$CaO,P_2O_3Cl_4,2(CH_3{\cdot}O{\cdot}CO{\cdot}C_6H_5)$:

Found: $CaO = 9{\cdot}75$; $P_2O_5 = 24{\cdot}97$; $Cl = 23{\cdot}25$; $C_8H_8O_2$ (by diff.) $= 47{\cdot}27$.

$CaO,P_2O_3Cl_4,2C_8H_8O_2$ requires $CaO = 9{\cdot}66$; $P_2O_5 = 24{\cdot}48$; $Cl = 24{\cdot}45$; $C_8H_8O_2 = 46{\cdot}90$ per cent.

Recrystallisation of $CaO,P_2O_3Cl_4,2(CH_3{\cdot}CO{\cdot}CH_3)$ *from Ethyl Acetate.*—One gram of freshly prepared

$$CaO,P_2O_3Cl_4,2(CH_3{\cdot}CO{\cdot}CH_3)$$

was dissolved by the aid of heat in about 15 c.c. of freshly distilled ethyl acetate. On cooling, there was an abundant separation of crystals, which on analysis gave the following figures, showing that they consisted of the ethyl acetate compound:

Found: $CaO = 12{\cdot}02$; $P_2O_5 = 29{\cdot}97$; $Cl = 29{\cdot}33$; $C_4H_8O_2$ (by diff.) $= 35{\cdot}29$.

$CaO,P_2O_3Cl_4,2C_4H_8O_2$ requires $CaO = 11{\cdot}57$; $P_2O_5 = 29{\cdot}34$; $Cl = 29{\cdot}31$; $C_4H_8O_2 = 36{\cdot}39$ per cent.

A similar experiment to the above was carried out, starting with the ethyl acetate compound, and recrystallising it from acetone. Crystals of the acetone compound resulted.

Experiments with Diethyl Oxalate and Ethyl Trichloroacetate.

It has already been mentioned (p. 1405) that from the behaviour of mixtures of lime and phosphoryl chloride at 25° it is probable that a compound, $CaO,3POCl_3$, is finally formed at that temperature by continued action of an excess of phosphoryl chloride on the compound $CaO,2POCl_3$ formed first of all.

The existence of the compound $CaO,3POCl_3$ has been confirmed by experiments carried out in presence of diethyl oxalate or ethyl trichloroacetate.

Lime dissolves fairly readily in a mixture of phosphoryl chloride and either of these esters when heated to 110°. It is advisable to use about ten parts by weight of phosphoryl chloride and thirty parts of ester to one part of lime. Solution of the lime is complete in about twenty-four hours, and on cooling well formed crystals slowly separate. About a week was required for complete separation from the oxalate solution, which yielded brilliant, rhombohedral prisms about 2 mm. long. Unfortunately, in spite of their appearance, these crystals did not consist of one compound only. It seems clear that what happens is as follows: First of all, either the compound $CaO,2POCl_3$ or $CaO,3POCl_3$ or a mixture of both is formed, according to the concentrations employed. Under the

influence of any traces of moisture present the oxalic ester derivative of the compound $CaO,P_2O_3Cl_4$ is formed from the compound $CaO,2POCl_3$. Moisture also acts on the compound $CaO,3POCl_3$, replacing chlorine by hydroxyl, with formation of compounds incapable of combining with organic esters, etc. It seems certain that the power of adding on these organic molecules is confined to the compounds of the general formula $MO,P_2O_3Cl_4$.

The results obtained in presence of oxalic and trichloroacetic esters can be explained in this way, but, owing to the complicated nature of the problem, it is unnecessary to give more than one analysis, and that mainly to show that the compound $CaO,3POCl_3$ is formed. The analysis refers to a well crystallised preparation from an oxalic ester experiment:

Found: $CaO = 10{\cdot}00$; $P_2O_5 = 37{\cdot}10$; $Cl = 52{\cdot}25$; $C_6H_{10}O_4$ (by titration with $KMnO_4$) $= 5{\cdot}19$; H_2O (by diff.) $= 7{\cdot}23$.

$$Ca : P = 1 : 2{\cdot}92.$$

Reaction between Lime and Phosphoryl Chloride in Presence of Ether.

In absolute ether lime reacts slowly with phosphoryl chloride to give the compound $CaO,2POCl_3$. This conversion can be effected in a sealed tube at 25° in somewhat longer than three weeks. A tube sealed up for that length of time gave a solid, which on analysis gave the following analytical figures:

Found: $CaO = 17{\cdot}42$; $P_2O_5 = 37{\cdot}15$; $Cl = 52{\cdot}11$. Deficit (ether) $= 5{\cdot}08$.

$$\text{Ratio: } Ca : P : Cl : \text{Ether} = 1{\cdot}24 : 2{\cdot}08 : 5{\cdot}88 : 0{\cdot}28.$$

Even with the above precautions a small quantity of the compound $CaO,P_2O_3Cl_4,2C_4H_{10}O$ appears to have been formed. The lime, moreover, is not completely converted.

If the reaction is carried out in a flask fitted with air condenser, and no special precautions are taken to ensure that the ether is absolutely free from moisture, the reaction occurring is much more energetic, the ether being sometimes caused to boil. Under these conditions larger proportions of the pyrophosphoryl chloride derivative are obtained; some of the compound $CaO,2POCl_3$ is, however, always present, and owing, moreover, to the fact that the ether compound begins to separate before all the lime has passed into solution it is difficult to obtain a pure product. The best preparation of the ether compound which we have obtained was got by the continued action of ether on an oxalic ester preparation. The final product of the action of ether consisted of small, brilliant rhombohedra. On solution in water it was evident that the crystals

contained considerable quantities of ether, although titration with permanganate showed that about 10 per cent. of the organic portion of the molecule was oxalic ester and not ether:

Found: $CaO = 12 \cdot 57$; $P_2O_5 = 31 \cdot 20$; $Cl = 29 \cdot 51$; $C_6H_{10}O_4 = 2 \cdot 66$; $C_4H_{10}O$ (by diff.) $= 30 \cdot 71$.

$CaO,P_2O_3Cl_4,2C_4H_{10}O$ requires $CaO = 12 \cdot 28$; $P_2O_5 = 31 \cdot 14$; $Cl = 31 \cdot 11$; $C_4H_{10}O = 32 \cdot 45$ per cent.

Reactions of Zinc, Cadmium, Cobaltous, and Cupric Oxides with Phosphoryl Chloride in Presence of Ethyl Acetate.

We have been unable to obtain any crystalline organic derivatives from the interaction of zinc oxide, phosphoryl chloride, and ethyl acetate.

In the case of cadmium oxide a white powder, seen to be crystalline under the microscope, was formed. It was quite insoluble in ethyl acetate, and the analysis gave the following figures:

	CdO.	P_2O_5.	Cl.	Ethyl acetate (by diff.).
Expt. I.	57·20	5·48	33·35	11·49
Expt. II.	49·11	7·25	31·96	18·88

The white solid is evidently a mixture of the compound

$$CdO,P_2O_3Cl_4,2(C_4H_8O_2)$$

and cadmium chloride (the latter apparently being combined with a variable amount of ethyl acetate of crystallisation). Experiment I, for example, can be apportioned as follows:

As $CdO,P_2O_3Cl_4,2(C_4H_8O_2)$ . . . $CdO = 4 \cdot 94$; $P_2O_5 = 5 \cdot 48$; $Cl = 5 \cdot 48$; $C_4H_8O_2 = 6 \cdot 78$, leaving (by difference) as $CdCl_2$ . . . $CdO = 52 \cdot 26$; $Cl = 27 \cdot 87$; $C_4H_8O_2 = 4 \cdot 71$ per cent.

Atomic ratio: Cd : Cl in the latter $= 1 : 1 \cdot 93$.

The reaction between cobaltous oxide, phosphoryl chloride, and ethyl acetate leads to the formation of a blue solution, from which nothing could be crystallised suitable for analysis, and of a blue solid which was simply cobalt chloride combined with some ethyl acetate.

With cupric oxide the course of the reaction is somewhat similar to that followed in the case of cadmium oxide. If large quantities of cupric oxide and phosphoryl chloride, in proportion to the ethyl acetate, are used, the reaction may be very vigorous. No copper passes into solution. The solid product appears to be more complex than in other cases, and is probably a mixture of the compounds CuP_2O_6, $CuO,P_2O_3Cl_4,2(C_4H_8O_2)$, and cupric chloride (combined with some ethyl acetate), as evidenced by the following analytical figures:

	CuO.	P_2O_5.	Cl.	Ethyl acetate (by diff.).
Expt. I.	38·88	24·58	33·59	10·52
Expt. II.	39·33	14·58	35·51	18·58

In conclusion, we wish to thank Messrs. R. Kingan, F. O. Rice, and E. T. Williams for assistance in preparing some of the compounds described above.

WILLIAM GOSSAGE LABORATORY,
UNIVERSITY OF LIVERPOOL.

CLIX.—*Some Reducing Actions of Mercury.*

By DAVID BORAR.

IT is stated by Kirchman (*Arch. Pharm.*, 1872, **200**, 203) that mercury is oxidised when agitated with a solution of potassium permanganate, mercurous oxide being formed if the solution is cold, and mercuric oxide if the solution is hot. At the suggestion of Dr. E. P. Perman I have investigated the action of mercury on potassium permanganate and on a number of other substances.

In all the experiments the solutions were agitated with mercury in a stoppered bottle, and at the ordinary room temperature unless otherwise stated. The mercury used was purified by the ordinary methods, and no doubt contained traces of other metals.

Potassium Permanganate.—No action takes place between dry potassium permanganate and mercury. In the presence of water, however, reduction of the permanganate takes place readily. With excess of mercury the reduction is complete, and the amount of potassium hydroxide formed from a known amount of permanganate was determined by titration with standard acid. Experiments were also made in which permanganate was in excess, and the amount required to oxidise a given weight of mercury was determined. The results of these experiments show that all the potassium in the permanganate is converted into potassium hydroxide, part of which seems to form adsorption compounds or unstable manganites with the manganese dioxide formed. As a mean of three experiments it was found that 1 gram of mercury reduces 0·519 gram of permanganate. These results indicate that the reaction between mercury and potassium permanganate takes place in accordance with the equation:

$$K_2Mn_2O_8 + 3Hg + H_2O = 2KOH + 2MnO_2 + 3HgO.$$

Potassium Dichromate.—Mercury does not reduce neutral solutions of potassium dichromate to any extent measurable by ordinary analytical methods. In the presence of hydrochloric acid, however, reduction takes place readily. Experiments were made in which excess of mercury was used, and others in which excess of dichromate was taken. The former showed that the dichromate was completely reduced to chromium chloride, and the latter that the amount of dichromate reduced by a given weight of mercury was constant providing that too large a quantity of hydrochloric acid was not taken. It was found as a mean of five experiments that 1 gram of mercury reduces 0·2452 gram of dichromate. The precipitate obtained in the various experiments was tested for mercurous chromate and mercuric chloride, neither of which could be detected, and the precipitate was found to consist of mercurous chloride only. From the equation:

$$K_2Cr_2O_7 + 6Hg + 14HCl = 2KCl + Cr_2Cl_6 + 3Hg_2Cl_2 + 7H_2O,$$

1 gram of mercury reduces 0·2456 gram of dichromate. The number found by experiment is in good agreement with this number. Hence the equation given probably represents the reaction which takes place.

Ferric Salts.—A solution of ferric chloride in water is readily reduced by mercury. Iron alum in the presence of hydrochloric acid is also reduced, but without the addition of hydrochloric acid reduction does not take place to any extent. Using mercury as reducing agent and titrating with standard dichromate in the usual way, the amount of iron in iron alum is found to be 11·61 per cent. The theoretical number is 11·59 per cent.

The amount of iron in hæmatite was determined by using mercury as reducing agent, and again using stannous chloride as reducing agent. The amount found was 91·30 per cent. by the first, and 91·16 per cent. by the second method.

Reduction takes place rapidly, especially if the solution is heated to 60—70°. The precipitate of mercurous chloride which forms during the process settles down rapidly from the hot solution, leaving the liquid clear. The presence, however, of comparatively large quantities of mercurous chloride does not affect the titrations appreciably.

The results obtained show that mercury may well be employed as a reducing agent for ferric compounds in the estimation of iron, and this method is less troublesome than the usual methods.

Potassium Persulphate.—On shaking a cold solution of potassium persulphate with mercury a slight, black precipitate was first formed, and then a white precipitate, which slowly changed to a lemon-yellow colour on keeping. The solution became acid, and

potassium sulphate remained in solution. In a hot solution, however, the yellow precipitate was formed almost immediately. This precipitate was insoluble in water, but soluble in dilute sulphuric acid. It decomposed on heating into mercury, oxygen, and sulphur dioxide. Mercuric sulphate readily gives the yellow basic sulphate with water, whereas mercurous sulphate does not, even on boiling. Hence the changes which take place are probably as follows:

$$2K_2S_2O_8 + 2H_2O = 4KHSO_4 + O_2.$$
$$4KHSO_4 + O_2 + 2Hg = 2K_2SO_4 + 2HgSO_4 + 2H_2O.$$
$$3HgSO_4 + 4H_2O = HgSO_4,2HgO,2H_2O + 2H_2SO_4.$$

Copper Sulphate.—A fairly good yield of cuprous chloride was obtained by shaking mercury with copper sulphate solution and excess of hydrochloric acid.

Nitrobenzene.—Mercury in the presence of hydrochloric acid was found to reduce nitrobenzene to aniline, but only to a small extent, even on heating.

The action of mercury was also tried on potassium nitrate in neutral and in acid solution, but no change could be detected. Solutions of potassium chlorate and sodium peroxide also had no action on mercury.

After the work of which this paper gives a brief account had been completed, my attention was called to a paper by Carnegie (Trans., 1888, **53**, 471) on the reduction of ferric salts by finely divided metals. Carnegie found that many metals, amongst them mercury, will reduce solutions of ferric salts, but does not point out that mercury can be used conveniently and possibly with advantage in the estimation of iron in ferric compounds. Previous work on the action of potassium permanganate on mercury, for example, that by Giles (*Chem. News*, 1867, **15**, 204), does not appear to have been carried out quantitatively.

In conclusion, my best thanks are due to Dr. E. P. Perman for many helpful suggestions and advice.

UNIVERSITY COLLEGE,
CARDIFF.

CLX.—*Electromotive Forces in Alcohol. Part I. Concentration Cells with Electrodes Reversible to Chlorine Ions.*

By ARTHUR LAPWORTH and JAMES RIDDICK PARTINGTON.

THE work described in the present paper was begun in connexion with the study of equilibria between electrolytes in alcohol, and in particular of the equilibrium between mineral acids, alcohol, and water.

The potential differences which it was desired to estimate being comparatively small ones, it was necessary, in the first instance, to ascertain whether it was possible to obtain consistent results with concentration cells, reproducible within not more than two or three millivolts, when anhydrous alcohol was used as cell liquid. The experiments were carried out with dissolved hydrogen chloride as electrolyte, for it was necessary to know as nearly as possible the transport numbers of its ions, for experiments to be undertaken later with the hydrogen electrode.

Numerous instances of measurements of potential differences in alcohol are to be found in the literature, but the few which appeared to bear directly on the points in question showed certain discrepancies which led us to re-investigate the subject. The following records are the most pertinent to the present inquiry.

Cattaneo (*Atti R. Accad. Lincei*, 1897, [v], **6**, i, 279) determined by Hittorf's method, the transport numbers for the chlorine ions in solutions of hydrogen chloride in various solvents, and obtained the following results:

In water, 0·224; ethyl alcohol, 0·205; methyl alcohol, 0·236; amyl alcohol, 0·240; glycerol, 0·237; ethyl alcohol + chloroform, 0·209; ethyl alcohol + ether, 0·218.

This worker compared these with the number 0·214 calculated by Kohlrausch from Hittorf's results with aqueous hydrochloric acid, and drew the conclusion that the influence of the solvent was almost inappreciable. More recent determinations, however, have shown that the value 0·214 for aqueous solution is considerably too high. Thus Bein (*Zeitsch. physikal. Chem.*, 1898, **21**, 1) obtained the value 0·166, Bogdan (*ibid.*, 1901, **37**, 673) 0·174, and Joachim (*Diss.*, Berlin, 1905) 0·167, whilst the results of Noyes and Sammet (*Zeitsch. physikal. Chem.*, 1903, **43**, 49) point to a value very close to 0·167 as the correct one (compare also Noyes and Kato (*J. Amer. Chem. Soc.*, 1908, **30**, 318). The conclusion drawn by Cattaneo thus appears to have a slender foundation.

Campetti (*Jahrb. Elektrochem.*, 1895, **1**, 22) determined the transport numbers of the anions in solutions of lithium chloride and silver nitrate in water, methyl alcohol, and ethyl alcohol. The values obtained for the former salt being 0·705, 0·64, and 0·700 respectively in these solvents.

Carrara (*Gazzetta*, 1896, **26**, i, 19; 1903, **33**, i, 241; compare also *Jahrb. Elektrochem.*, 1897, **3**, 12 and 13) obtained limiting values for conductivities of numerous salts, in water and in methyl alcohol, which were independent of concentration. Using Campetti's values for transport numbers in methyl alcohol, the mobilities of numerous ions in this solvent at 25° were calculated, and the following may be recorded here: $Li^{\bullet}$, 27·83; $Na^{\bullet}$, 37·33; $K^{\bullet}$, 46·10; $H^{\bullet}$, 85·53 or 82·5. These were virtually independent of concentration, and their relative values were affected by the change of solvent from water to methyl alcohol, to an extent not exceeding 10 per cent. in any instance.

Dempwolff (*Physikal. Zeitsch.*, 1904, **5**, 637) measured by Hittorf's method, and by the electromotive forces of concentration cells, the transport numbers of the ions of the haloid salts of potassium in methyl alcohol, and found throughout much the same behaviour as with aqueous solutions, but the number for the anion was consistently and considerably lower than that for the aqueous solutions.

Völlmer (*Ann. Phys. Chem.*, 1894, [iii], **52**, 328) measured with great care the conductivities of a number of salts in ethyl and methyl alcoholic solution. His results show that over the range of temperature followed, the limiting value for a given salt in methyl alcohol and ethyl alcohol at 18° may be calculated roughly from that in water at the same temperature by multiplication with the factors 0·73 and 0·34 respectively. The temperature-coefficients were hardly different from the temperature-coefficients of the fluidities of the respective solvents.

The present authors have experimented with two types of concentration cells containing hydrogen chloride in absolute alcohol as electrolyte; these contained electrodes of mercury and silver respectively, with mercurous chloride and silver chloride as depolarisers.

It was to be anticipated that the use of an easily oxidisable solvent such as alcohol would probably lead to experimental difficulties not met with when water is employed. Nevertheless, it was finally found possible, with the precautions described in the practical section of this paper, to obtain consistent potential differences, and to reproduce these with solutions of given concentrations within three millivolts at most.

The values for the transport numbers of the ions as calculated

from these results showed a very striking divergence from those obtained with aqueous solutions, that for the anion being about 0·35, in contrast to 0·17, as is obtained with aqueous hydrochloric acid. There are, however, many reasons for believing that this result is not very far from the correct one, as the following considerations may serve to show, and these give the authors confidence in recording the results of their experiments at the present juncture.

In the first instance may be cited the results of Carrara already referred to, from which a value for the transport number for chloridion in methyl-alcoholic hydrogen chloride can be calculated as 0·367. It is remarkable that so striking a result should not have attracted considerable interest as having an obvious bearing on the solvate theory; even in the comprehensive treatise of Jahn ("Grundriss der Electrochemie," 1905) the principal numerical results obtained by Carrara are given, but no special attention is drawn to the anomalous value of the relative mobility of the hydrogen ion.

Secondly, the work of Völlmer, already dealt with, on conductivities in absolute ethyl alcohol, probably attained a high degree of accuracy, and his numbers can hardly be explained on any assumption other than that the relative velocities of most ions, in all the salts examined by him, are nearly the same in water, methyl alcohol, or ethyl alcohol, although the absolute velocities are, of course, entirely different. If this be the correct interpretation of his results, then the transport numbers for the ions of the salts are nearly the same in the three solvents, and the absolute value of the mobility of chloridion in ethyl alcohol may be nearly estimated by multiplying the molecular conductivity of lithium or sodium chloride at infinite dilution in that solvent by the transport number of chloridion in water.

The values of λ_{∞} obtained by Völlmer for these two salts were:

	λ_{∞}.		
	In water at 18°.	In ethyl alcohol at 18°.	In ethyl alcohol. at 25°.
Sodium chloride	103·0	35·9	40·7
Lithium chloride	96·0	32·1	36·4

The numbers in the last column are calculated by means of the mean temperature-coefficient determined by Völlmer; multiplying these by the transport numbers of chloridion in aqueous solutions of these two salts, namely, 0·600 and 0·661 respectively (Kohlrausch, 1900, 1902), the values 24·4 and 24·10 are obtained for the mobility of chloridion in alcohol at 25°; subtracting the mean of these, namely, 24·25, from 66·5, the value of λ_{∞} for alcoholic hydrogen chloride at 25° obtained from measurements recorded in the present

paper, the number 42·25 is obtained for the mobility of the hydrogen ion in anhydrous alcohol, and the transport number for chloridion becomes

$$\frac{24 \cdot 25}{66 \cdot 5} = 0 \cdot 365.$$

Extrapolation from the data given by Goldschmidt and Udby (*Zeitsch. Elektrochem.*, 1901, **15**, 5) leads to 75 as the approximate value of λ_{∞} for alcoholic hydrogen chloride, and applying this in the foregoing manner, the transport number assumes the value 0·323.

Again, using the transport number, 0·71, obtained by Campetti from direct measurements for chloridion in lithium chloride in alcohol, the mobility of chloridion in alcohol at 25° becomes 25·7, and the transport number in alcoholic hydrogen chloride 0·387.

Lastly, it may be added that experiments in this laboratory on the use of the hydrogen electrode in solutions in anhydrous alcohol have given results which point to a value very near 0·32.

Experimental.

The absolute alcohol was prepared by distillation from a proved excess of calcium ethoxide in the manner described in a previous communication (Lapworth and Partington, Trans., 1910, **97**, 24). Hydrogen chloride, prepared from well-dried salt and sulphuric acid, was passed through two sulphuric acid drying towers into the alcohol contained in a special apparatus of Jena glass, in which all the connexions were made with ground-glass joints. The exit tube of this apparatus was connected with a sulphuric acid drying tower, and the receiving flask was cooled during the absorption of the gas. The entrance tube of this apparatus was provided with a stopcock, and afterwards served as a syphon for withdrawing the solution from the flask which remained in attachment to the drying-tower, so that access of moisture was avoided.

The acid obtained was of approximately normal strength, a nearly decinormal acid being prepared from it by transferring a portion to a similar apparatus and diluting with absolute alcohol. This operation, and the subsequent filling of the electrodes, were performed as rapidly as possible, to avoid entrance of atmospheric moisture.

The form of concentration cells used is shown in the figure. Two types were employed:

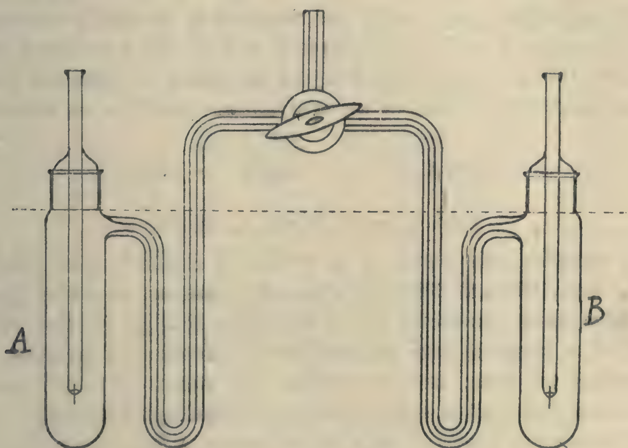
(1) $Hg,Hg_2Cl_2,[HClAlc.]_1 | [HClAlc.]_2,Hg_2Cl_2,Hg.$

(2) $Ag,AgCl,[HClAlc.]_1 | [HClAlc.]_2,Hg_2Cl_2,Hg.$

The tubes *A* and *B* were about 6 cm. long and 1·5 cm. wide. In

the calomel cell the electrodes consisted of platinum wires sealed through glass tubes and dipping under the surface of redistilled mercury. About 0·5 cm. of calomel, previously carefully purified as usual by shaking with water and mercury, washing with alcohol, and drying, was placed over the mercury, and the tubes filled with the alcoholic hydrogen chloride solutions by means of the three-way tap *C*. This tap was greased with vaseline, and kept closed except when a reading was taken. The cell was immersed, to the level shown by the dotted line, in a thermostat at 25°.

In making the cell with silver electrodes, some difficulty was at first experienced in fixing the silver wires, attached to silver plates, in the electrodes, because sealing-wax (which is an admirable material in the case of aqueous solutions) cannot be used in contact



with alcohol. It was found possible, with experience, to cement a silver wire into the constricted part of a glass tube by means of silver chloride fused on with a spirit lamp. The cell was otherwise made up in a manner similar to the calomel cell. In all cases, ground-glass connexions only were used.

The electromotive force measurements were made by means of a potentiometer apparatus consisting of a carefully calibrated platinum-iridium wire with tapping contacts of the same alloy, a Weston normal element, and an Ayrton-Mather moving coil galvanometer. With this apparatus, potential measurements correct to at least 0·5 millivolt could be made.

A number of preliminary measurements at the ordinary temperature with commercial absolute alcohol, of about 99·6 per cent. strength, showed that, with the solutions used, cells of the above

types rapidly attained a steady potential, undisturbed by shaking, and reproducible within fairly narrow limits.

In some cases (and also in all cases when perfectly dry alcohol was used) the potential attained a steady value somewhat slowly. This continuous change of potential to a constant final value, doubtless due to slow saturation of the solutions with the depolariser, was totally different from the irregular fluctuation of potential appearing when an electrode is irreversible. These results make it exceedingly probable that electrodes of the types described functionate in a reversible manner.

It was found that with alcoholic solutions of hydrogen chloride of normal strength, the calomel in the cells was rapidly darkened, a change which also occurred, much more slowly, even with decinormal solutions. A portion of the liquid was tested for aldehyde with a negative result, and the reaction is probably analogous to that investigated by T. W. Richards and E. H. Archibald (*Zeitsch. physikal. Chem.*, 1902, **40**, 385) in the case of aqueous solutions, and formulated by them as an equilibrium reaction as follows:

$$\begin{array}{ccccc} x\mathrm{HCl} & \rightleftarrows & x\mathrm{H}^{\cdot} + x\mathrm{Cl}' & & \\ \mathrm{Hg_2Cl_2} & \rightleftarrows & \mathrm{HgCl_2} & + & \mathrm{Hg} \\ \downarrow\uparrow & & \downarrow\uparrow & & \uparrow\downarrow \\ \mathrm{Hg_2Cl_2}\text{ solid} & & \mathrm{HgCl_{2+x}} & & \mathrm{Hg}\text{ liquid} \end{array}$$

The complex ion $HgCl_{2+x}$ is probably $HgCl_4''$ (Le Blanc and Noyes, *ibid.*, 1890, **6**, 389). We found, however, that the darkening of the calomel produced no measurable change in the potential, provided a large excess of unaltered calomel was present. It is interesting to note, however, that the effect is very marked in alcoholic solution with concentrations of hydrogen chloride which in aqueous solution produce very little change, a fact which is probably connected with the greater activity of the acid in alcoholic as compared with aqueous solution.

It was also found that the potential of the silver cell was the same, whether measured in complete darkness, in orange light, or in diffused daylight, although in the latter case a darkening of the silver chloride occurred.

A comparison of results given in detail below indicates that the mean potentials of the calomel and of the silver cells are not markedly different, the former, however, being more regular.

Some experiments were carried out with solutions of hydrogen chloride in absolute alcohol which had not been dried over calcium. The results agreed with those obtained with calcium-dried alcohol, but the potentials assumed a steady value more rapidly in the former case.

Some preliminary experiments have been made with the cells

immersed in ice, and the results are given below. In both types of cell the effect of cooling was to produce at first a rise and then a fall of potential, the final value being in some cases slightly greater and in others slightly less than the potential of the cell at 25°. These curious results are possibly connected with the changes of solubility of the depolarisers, leading to a readjustment of equilibrium which occurs only very slowly. Further, the silver chloride is also a colloidal substance, and this would doubtless explain the rather less concordant results obtained with those cells in which it was used.

Results.

In all cases the first reading was taken about fifteen minutes after setting up the cell.

The time is given in hours after the observations were begun; the potentials are in volts.

The arrow indicates the direction of the positive current inside the cell.

(1) $Hg,Hg_2Cl_2,[1·114N\text{-}HCl] \xrightarrow{\quad} [0·1021N\text{-}HCl],Hg_2Cl_2,Hg$.

Time.	Potential.	Time.	Potential.
0·00 hours	0·0600 volt	Reading taken at 0°.	
0·15 ,,	0·0601 ,,	25·0 hours	0·0601 volt
0·5 ,,	0·0605 ,,	Readings at 25° resumed.	
2·25 ,,	0·0604 ,,	25·5 hours	0·0619 volt
20·0 ,,	0·0558 ,,	50·0 ,,	0·0602 ,,

(2) $Ag,AgCl,1·114N\text{-}HCl \mid 0·1021N\text{-}HCl,AgCl,Ag$

Time.	Potential.	Time.	Potential.
0·0 hours	0·0520 volt	Reading taken at 0°.	
0·4 ,,	0·0520 ,,	29·7 hours	0·0596 volt
3·4 ,,	0·0543 ,,	Reading at 25° resumed.	
23·15 ,,	0·0536 ,,	53·0 hours	0·0576 volt
29·4 ,,	0·0528 ,,		

(3) $Ag,AgCl,0·7867N\text{-}HCl \mid 0·0731N\text{-}HCl,AgCl,Ag$.
(*With Alcohol dried over Calcium.*)

Time.	Potential.	Time.	Potential.
0·0 hours	0·0417 volt	90·0 hours	0·0543 volt
17·5 ,,	0·0466 ,,	90·5 ,,	0·0543 ,,
22·0 ,,	0·0467 ,,	Readings taken at 0°.	
25·0 ,,	0·0502 ,,	117·75 hours	0·0480 volt
43·0 ,,	0·0543 ,,	122·0 ,,	0·0491 ,,

(4) $Hg,Hg_2Cl_2,0{\cdot}7867N\text{-}HCl\,|\,0{\cdot}0731N\text{-}HCl,Hg_2Cl_2,Hg$.
(*With Alcohol dried over Calcium.*)

Time.	Potential.	Time.	Potential.
0·0 hours	0·0371 volt	71·1 hours	0·0558 volt
3·14 ,,	0·0416 ,,	Readings taken at 0°.	
23·64 ,,	0·0568 ,,	95·10 hours	0·0567 volt
70·14 ,,	0·0569 ,,	100·35 ,,	0·0554 ,,

The discrepancy of 6 millivolts between the *E.M.F.*'s of cells 3 and 4 at 0°, prepared with solutions having the same concentration in the two cases, is in marked contrast to the identity of the values at 25°, and has not yet been accounted for. As a rule, cells prepared with such solutions gave almost identical and steady values when kept at 25°.

In the following tables are given the constant *E.M.F.*'s of some cells as measured at 25°, and the corresponding values deduced for the transport number $(1-n)$ for chloridion in anhydrous alcoholic hydrogen chloride. The values for $(1-n)$ vary between 0·32 and 0·41 with cells prepared with acids having different concentrations, a variation which is probably not unreasonably large when the uncertainties in the calculation of boundary potentials are considered, and due regard is paid to the practical difficulties arising from the chemical instability of alcohol as contrasted with water.

The transport numbers were calculated by the usual equation:

$$E = 2n\,\frac{RT}{F}\log_e\frac{a_1c_1}{a_2c_2},$$

where E = electromotive force,
n = transport number of the positive ion,
R = the gas constant,
T = absolute temperature,
F = charge per gram-ion,
c_1, c_2 = concentrations of the electrolyte,
a_1, a_2 = degrees of dissociation in the two solutions.

If λ_1, λ_2 are the molecular conductivities for concentrations c_1, c_2, we have:

$$a_1/a_2 = \lambda_1/\lambda_2,$$

and, with the ordinary units:

$$E = 2n \times \frac{8{\cdot}316 \times 298 \times 2{\cdot}3026}{96540}\log_{10}\frac{\lambda_1c_1}{\lambda_2c_2}\ \text{volts}$$

In one experiment:

$$E=0{\cdot}0588;\ c_1=1{\cdot}114n;\ c_2=0{\cdot}102n;$$
$$\lambda_1=16{\cdot}75;\ \lambda_2=33{\cdot}8;$$

$$\therefore\ 2n = \frac{0{\cdot}0588 \times 96540}{8{\cdot}316 \times 298 \times 2{\cdot}3026 \times \log_{10}\dfrac{1{\cdot}114 \times 16{\cdot}75}{0{\cdot}102 \times 33{\cdot}8}},$$

$$\therefore 2n \quad = 1{\cdot}3572,$$
$$\therefore 1-n = 0{\cdot}3214.$$

(1) *With Calomel Electrodes.*

c_1.	a_1.	c_2.	a_2.	E (volt).	$1-n$
0·06408	0·550	0·00641	0·755	0·0602	0·41
1·114	0·255	0·1021	0·511	0·0564	0·35
1·114	0·255	0·1021	0·511	0·0593	0·32
0·7867	0·289	0·0731	0·545	0·0565	0·37
				Mean...............	0·36

(2) *With Silver Electrodes.*

c_1.	a_1.	c_2.	a_2.	E (volt).	$1-n$.
0·7867	0·289	0·0731	0·545	0·0543	0·39
1·114	0·255	0·1021	0·511	0·0538	0·38
				Mean...............	0·385

Mean of both series = 0·37.

Needless to say, perhaps, numerous results obtained before sufficient experience with such cells had been gained, or others in which definite constancy was not reached, are not included in the above list, but, even including these, the extreme of all values for $(1-n)$ throughout lay between 0·28 and 0·47, and the value 0·37 may be regarded as the most probable one deduced from the whole of the experiments.

Conductivities of Alcoholic Hydrogen Chloride.

Some measurements of the conductivities of solutions of hydrogen chloride in alcohol at 25° have been carried out by Goldschmidt and Udby (*Zeitsch. Elektrochem.*, 1909, **15**, 5) with the following results:

Concentration.	λ_{25}.
$0{\cdot}1N$	34·1
$0{\cdot}05N$	39·0
$0{\cdot}025N$	44·7
$0{\cdot}0125N$	50·2
$0{\cdot}00625N$	55·6

The range of dilutions used by these observers is unfortunately

too narrow to allow of more than a very rough estimation of the limiting value of the conductivity at infinite dilution.

Baly, Burke, and Marsden (Trans., 1909, **95**, 1100) have carried out measurements of the conductivity of alcoholic hydrogen chloride at 15°, from which they find the values 21·86 and 43·10 for the molecular conductivities at decinormal concentration and at infinite dilution respectively. From these numbers, however, it would appear possible that Völlmer's rule for the temperature-coefficient of salts, already referred to, cannot be extended to acids. Experiments to test this point are being made in this laboratory.

It was therefore thought desirable to redetermine the molecular conductivities at 25°, up to such dilutions that a limiting value could be found with some probability of accuracy. The results were, for the most part, identical with the numbers of Goldschmidt and Udby, except at the highest dilution, where somewhat lower values were obtained. The measurements were made by the Kohlrausch method in a small cell with platinised platinum electrodes which was almost completely filled with solution, and closed by a ground stopper. The admission of air causes a steady rise in conductivity, which is probably due to oxidation of the alcohol (compare Cohen, *Zeitsch. physikal. Chem.*, 1898, **25**, 1). With the above precautions, and frequent shaking of the cell, consistent numbers were finally obtained up to $V=10^6$.

Concentration.	λ at 25°.	λ from smoothed curve.
0·6341n	20·42	20·24
0·06408n	36·57	36·57
0·01282n	45·56	47·00
0·00583n	52·35	50·95
0·001025n	57·00	57·00
[0·0000n	—	66·5]

The value $\lambda_{\infty}=66·5$ was obtained by Kohlrausch's method of extrapolation on the graph of λ against the cube-root of the concentration, which Philip and Courtman (Trans., 1910, **97**, 1266) have shown to apply accurately to alcoholic solutions of tetramethylammonium iodide and potassium iodide.

Summary.

(1) The electromotive forces of the concentration cells:

(*a*) $Hg,Hg_2Cl_2,[HClAlcohol]_1|[HClAlcohol]_2,Hg_2Cl_2,Hg$.

(*b*) $Ag,AgCl,[HClAlcohol]_1|[HClAlcohol]_2,AgCl,Ag$,

which appear to fulfil the conditions for reversibility, and as a rule give nearly constant values at 25°, have been studied.

(2) The results indicate that the ratios of the mobilities of hydrions and chloridions are quite different in alcohol and in water,

the transport number of chloridion in alcohol being about 0·37, as contrasted with 0·16 in aqueous solution.

(3) It is shown that a number not very different from this is also indicated by a variety of other considerations.

(4) The transport numbers of most ions other than hydrion do not appear to be greatly affected by a similar change of solvent.

The work described in the present paper is being continued, and, in particular, examination is being made of the effect of change of temperature on cells of the kinds herein dealt with.

The influence of water on the potential of these cells is also under investigation, as it is hoped that in this direction evidence as to whether the chlorine ion unites with this substance may be forthcoming. Positive evidence in the case of the hydrogen ion has already been obtained in this laboratory by the use of the hydrogen electrode.

The authors' thanks are due to Mr. R. T. Hardman for valuable assistance during the course of the work, and they also desire to acknowledge their indebtedness to the Royal Society for a grant from the Government Grant Research Fund which defrayed much of the cost of the investigation.

SCHUNCK LABORATORY,
THE UNIVERSITY, MANCHESTER.

CLXI.—*Equilibrium in the System: Ethyl Alcohol, Acetic Acid, Ethyl Acetate and Water, and its Apparent Displacement by Hydrogen Chloride.*

By WILLIAM JACOB JONES and ARTHUR LAPWORTH.

THE equilibrium constant $K = \frac{[H_2O][CH_3\cdot CO_2\cdot C_2H_5]}{[C_2H_5\cdot OH][CH_3\cdot CO_2H]}$ is known to be approximately 4 for the homogeneous liquid system over a very wide range of temperature, its value being but slightly affected by the addition of small quantities of catalysts, by alterations in the relative amounts of the constituents, or by the use of various indifferent solvent media.

Whilst the activity of hydrogen chloride in alcohol is greatly diminished by small amounts of water, it is but imperceptibly affected by acetic acid or by ethyl acetate; hence, if the variations in the availability of hydrogen chloride are, in fact, due to com-

bination of the latter with water, then hydrogen chloride, when passed into an equilibrium mixture of water, ethyl acetate, alcohol, and acetic acid, should unite almost exclusively with the water when the latter is there in considerable quantity. The experience of Berthelot and Péan de Saint-Gilles with indifferent solvents would lead to the conclusion that the value of K, corrected for the quantities of the four constituents removed by the hydrogen chloride and rendered inert, would still remain nearly constant. The present paper describes measurements of this kind, which show that as the ratio of the amount of water existing in equilibrium to the amount of hydrogen chloride falls, the value of ψ (the apparent value of K calculated on the assumption that the water in the system is entirely in the free state) rises from 4 to 8 at least, indicating clearly that some of the water present combines with the hydrogen chloride. Further, assuming that this apparent variation in the "constant" is, as suggested, due to hydrate formation, it may be calculated that, roughly, two molecules of water associate with each molecule of hydrogen chloride present, although the existence of higher hydrates in a partly dissociated condition is not excluded.

Records of earlier work on somewhat similar lines exist; thus the state finally attained in the liquid system:

$$C_2H_5{\cdot}OH + H_2SO_4 \rightleftharpoons C_2H_5{\cdot}SO_4H + H_2O,$$

has recently been the subject of investigations by Zaitschek (*Zeitsch. physikal. Chem.*, 1897, **24**, 1) and by Kremann (*Monatsh.*, 1910, **31**, 245, 1031, 1051). Zaitschek found that at equilibrium the quantity $\frac{[C_2H_5{\cdot}OH][H_2SO_4]}{[C_2H_5{\cdot}SO_4H][H_2O]}$ varied greatly if the values for the total concentration of water and sulphuric acid present were introduced. Assuming, however, that the sulphuric acid present was wholly in the form of the hydrate $H_2SO_4,2H_2O$, a constant value for the above expression was obtained. On the other hand, Kremann found values $1{\cdot}7 \pm 0{\cdot}2$ without making any allowance for the presence of hydrates, and concluded that the water in the form of hydrates is almost as effective a hydrolyst as is free water, and, further, that hydrated sulphuric acid combines with alcohol as readily as does the non-hydrated acid. In the light of what is now known of the behaviour of hydrogen chloride, however, Kremann's views appear most improbable, and the matter would seem to be more plausibly explained by assuming that at the fairly high temperatures he used the hydrates undergo more or less nearly complete thermal dissociation, for the basic affinity of water as compared with that of alcohol falls off very rapidly with rise in temperature. The case dealt with in the present paper is much

more simple in character, and the results appear capable of no other explanation than that the hydrogen chloride removes water preferentially from the system water, alcohol, acetic acid, and ethyl acetate.

It is of interest to note that Berthelot and Péan de Saint-Gilles (*Ann. Chim. Phys.*, 1863, [iii], **68**, 225) record an experiment showing that the presence of barium chloride affects to a marked extent the proportion of benzoic ester hydrolysed by water at 200°, and add: "Peut-être l'affinité du chlorure de barium pour l'eau concourt-elle à affaiblir l'action decomposante de cette dernière substance" (*loc. cit.*, p. 248).

Experimental.

The procedure in each of the experiments was as follows. Ordinary test-tubes were subjected to the action of a current of steam, dried, constricted near the open end, and weighed. By means of narrow thistle-funnels passed through the constriction in the test-tube, quantities of ethyl acetate and hydrochloric acid were introduced. The tube was weighed after each such addition, and then sealed off at the constriction, when it was immersed in a bath, kept at $25^\circ \pm 0{\cdot}02^\circ$, and frequently shaken. The mixture became homogeneous after about one to two hours when $7{\cdot}268N$-hydrochloric acid was used, and the tubes were broken and their contents analysed after forty to fifty-eight hours; in experiments Nos. 1 and 4, however, thirty-five days elapsed before they were removed from the bath. When $0{\cdot}1185N$-hydrochloric acid was employed, complete admixture did not occur until after nearly three weeks, and in such cases the tubes were not removed before thirty-six days. The dried tubes were finally broken in excess of carefully neutralised sodium acetate solution, which was then diluted to a litre, portions of 100 c.c. being taken and titrated against standard baryta solution, with phenolphthalein as indicator. The amount of hydrogen chloride which remained was checked by means of standard silver nitrate. The diluting water, sodium acetate solution, and nitric acid were tested, and found to be free from chloride. Kahlbaum's purest ethyl acetate was used throughout, and the baryta solutions used for titration were frequently standardised against a $0{\cdot}1185N$-hydrochloric acid solution which had been analysed gravimetrically. The $7{\cdot}268N$-hydrochloric acid solution was standardised immediately before each measurement. All the measuring vessels used were either standard or had been calibrated. The results of the experiments are summarised in the table.

In line *A* are given the numbers of the experiments.

" " *B* " " weights of ethyl acetate taken.

In line C are given the weights of $7 \cdot 268N$-hydrochloric acid.
" " D " " weights of $0 \cdot 1185N$-hydrochloric acid.
" " E " " amounts of hydrogen chloride taken in gram-molecules.
" " F " " amounts of hydrogen chloride found at the end of the experiment.
" " G " " total titres (acetic acid plus hydrogen chloride) in c.c. of normal acid.

In lines H, K, and L are given the total apparent number of gram-molecules of acetic acid (and alcohol), of water, and of ester, respectively, found at equilibrium.

In line R are given the ratios $[H_2O(\text{total})]/[HCl]$ in each case.
" " S " " values of ψ.

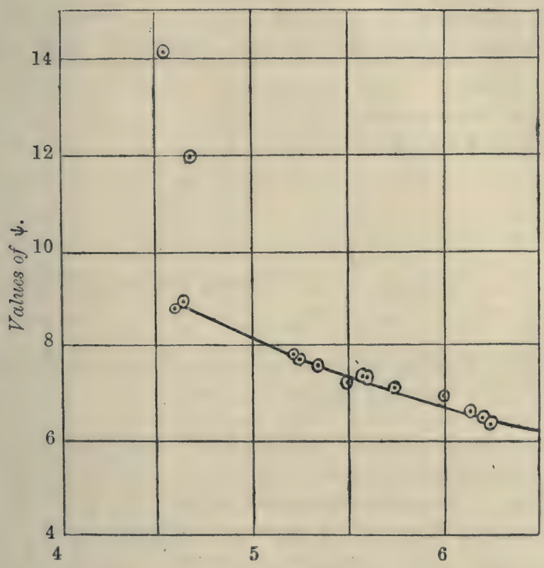
$$\psi = \frac{[H_2O\ (\text{total})][CH_3{\cdot}CO_2{\cdot}C_2H_5]}{[CH_3{\cdot}CO_2H][C_2H_5{\cdot}OH]}.$$

Two other experiments were carried out, giving $\psi = 14 \cdot 19$ and $11 \cdot 98$ respectively; there was doubtless in both these cases some slip in the initial weighings. The apparent value, $\psi = 4 \cdot 35$, experiment No. 14, corresponds with the formation of 0·6761 gram-molecule of ethyl acetate and of water from 1 gram-molecule of acetic acid and of ethyl acetate. Berthelot and Péan de Saint-Gilles (*loc. cit.*) found that, at 9°, 1 gram-molecule of ethyl alcohol and of acetic acid combined to form 0·665 gram-molecule of ethyl acetate and of water, in the absence of hydrogen chloride ($[H_2O]/[HCl] =$ infinity).

The diagram shows the variation in the value of ψ, the apparent value of the equilibrium constant with variation in the value of the ratio $[H_2O(\text{total})]/[HCl]$, where the square brackets refer to relative molecular concentration at equilibrium. The two very doubtful results obtained are included, although having regard to their quite anomalous position on the diagram, it would probably have been legitimate to discard them.

A ...	1	2.	3.	4.	5.	6	7.	8.
B ...	12·3121	11·7921	11·3334	10·4887	11·1817	8·0458	7·0384	10·1819
C ...	2·0154	1·9992	3·9524	3·9337	4·6554	6·1489	4·2332	6·4593
D ...	—	—	—	—	—	—	—	—
E ...	0·01272	0·01265	0·02494	0·02482	0·02938	0·03880	0·02671	0·04076
F ...	0·0129	0·01264	0·0255	0·0255	0·0300	0·0397	0·0273	0·0419
G ...	40·04	39·30	63·68	62·05	71·27	78·81	58·20	87·32
H ...	0·02732	0·02665	0·03874	0·03723	0·04189	0·04001	0·03149	0·04656
K ...	0·05863	0·05884	0·1303	0·1306	0·1571	0·2230	0·1491	0·2295
L ...	0·1125	0·1073	0·0900	0·0820	0·0851	0·05142	0·04849	0·0690
R ...	4·61	4·65	5·22	5·26	5·35	5·75	5·58	5·63
ψ......	8·83	8·90	7·81	7·73	7·62	7·17	7·29	7·30

A ...	9.	10.	11.	12.	13.	14.	15.
B ...	7·4224	5·811	5·3922	5·6624	3·9716	11·5222	11·0326
C ...	5·8523	7·6946	9·3930	11·0293	8·6004	—	—
D ...	—	—	—	—	—	4·4614	6·0886
E ...	0·03693	0·04855	0·05926	0·06958	0·05423	0·000528	0·000720
F ...	0·0371	0·0490	0·0610	0·0706	0·0542	—	—
G ...	74·42	84·35	96·02	109·8	83·43	57·38	63·04
H ...	0·03749	0·03580	0·03676	0·0402	0·02917	0·05685	0·06232
K ...	0·2127	0·2933	0·3648	0·4316	0·3386	0·1898	0·2744
L ...	0·04684	0·03032	0·02452	0·02414	0·01596	0·0741	0·06304
R ...	5·76	6·04	6·16	6·20	6·24	359·7	381·0
ψ ...	7·09	6·94	6·62	6·45	6·35	4·35	4·45



Experiments with solutions, 1·000 gram of which contained 0·000132 gram-molecule of hydrogen chloride and 0·0068 gram-molecule of calcium chloride, were also begun, but it was found that they did not become homogeneous, even after six months, or when subsequently heated at 100° for twenty hours.

Summary.

(1) Measurements have been made of the total quantities of alcohol, acetic acid, ethyl acetate, and water at equilibrium in presence of varying proportions of hydrogen chloride.

(2) No appreciable amount of ethyl chloride is formed under the conditions of the experiments.

(3) The apparent value for the equilibrium constant varies from 4 to over 8, as the concentration of the hydrogen chloride increases.

(4) The apparent diminution in the active mass of the water corresponds nearly with the formation of a compound having the formula $HCl,2H_2O$, or of compounds having that mean composition.

It is intended to use the above methods in certain other cases, and especially to examine the influence of some salts on the value of the equilibrium constant in systems containing water.

The authors desire to state that the expenses of this investigation were partly defrayed by a grant from the Government Grant Research Fund of the Royal Society, for which their thanks are due.

Chemical Laboratories.
University of Manchester.

CLXII.—*The Purification and Properties of Acetic Acid.*

By William Robert Bousfield, M.A., K.C., and Thomas Martin Lowry, D.Sc.

On account of its convenient melting point, boiling point, and other physical properties, acetic acid has been used extensively as a material for physico-chemical investigations, such as those of Oudemans on the density of solutions (*Zeitsch. Chem.*, 1866, **2**, 150), of Ramsay and Young on vapour pressures (*Phil. Trans.*, 1884, **175**, 469) and on vapour densities (Trans., 1886, **49**, 790), and of de Visser on the influence of pressure on melting point (*Rec. trav. chim.*, 1893, **12**, 101).

It has frequently been assumed that a pure acid can be obtained merely by freezing the liquid and pouring away the unfrozen mother liquor from which the crystals have separated. In recent years this assumption has been proved to be false, and it has become a matter of some importance to obtain a more efficient method of purifying the acid, and to redetermine several of its physical constants by measuring the properties of the purified material. It is, indeed, remarkable that in spite of its extensive use in cryoscopy, doubt should still exist as to the true freezing point of the acid; still greater uncertainty is found in the case of other physical properties, and the conductivity data appear to be entirely untrustworthy.

Maximum Acetic Acid as a Standard of Electrolytic Conductivity.

Our attention was first directed to the problem nearly ten years ago, when an attempt was made to utilise the acid as a standard of electrolytic conductivity. The electrolytes usually employed for calibration include not only solutions made up to a measured concentration, such as 21 per cent. N-, $N/10$-, $N/50$-, and $N/100$-solutions of potassium chloride, but also saturated solutions, such as those of salt and gypsum, and solutions having a maximum conductivity, such as those of sulphuric acid, magnesium sulphate, and acetic acid. The saturated solutions cannot be regarded as very satisfactory, on account of their slowness in recovering from changes of concentration consequent upon exposure to variable atmospheric temperatures; but solutions of maximum conductivity are very convenient to use, as their conductivity is not appreciably affected by small errors in concentration. Two of these solutions,

Sulphuric acid..................	30 per cent.	$\kappa_{18}=0·7398$ mho.
Magnesium sulphate	17·4 per cent.	$\kappa_{18}=0·4922$ mho.

are in constant use, but the third,

Acetic acid	16 per cent.	$\kappa_{18}=0·0016$ mho.,

proposed by Kohlrausch in 1876, has been abandoned as untrustworthy, in spite of the great convenience that would attend its use in the calibration of vessels of small resistance capacity.

The reason for this abandonment was at once clear when we attempted to use the acid for calibration, taking for its maximum conductivity the value $\kappa_{18}=0·001619$ given in Kohlrausch and Holborn's "Leitvermögen der Elektrolyte," p. 155. In the case of one particular vessel, the values obtained for the resistance capacity were as follows:

KCl 21 per cent.	1·969.	KCl $N/10$	1·966.	NaCl (saturated)	1·971.
KCl N	1·971.	KCl $N/100$	1·969.	Acetic acid	1·944.

The last observation, unless due to some unsuspected error, showed that the conductivity of the acid was considerably higher than had previously been supposed, namely 1640 gemmho, instead of 1619. A second sample of acid which had been frozen and drained behaved in the same way, giving a maximum conductivity of 1645 gemmho. As these values differed so seriously from those hitherto accepted as correct, a systematic investigation was undertaken in order to ascertain the source of the discrepancy, as well as the true value for the maximum conductivity of the acid. In this investigation we had the advantage of using a far more delicate test of the purity of the acid than those which had been employed

previously, since the course of the purification could be followed with ease and certainty by measuring the maximum conductivity of the different samples.

Fractional Distillation of Acetic Acid.

Fractional distillation showed at once the presence of substances of high boiling point and low conductivity and of low boiling point and high conductivity. An attempt was therefore made to fractionate a pure acid from a large sample of about 10 litres. The first distillation gave eight fractions, ranging in maximum conductivity from 1833 to 1655 gemmho. When redistilled with a 12-pear still-head, the first portion (κ 1833) gave fractions ranging in maximum conductivity from 2030 to 1688 gemmho, whilst the last portion (κ 1655) gave fractions ranging from 1714 to 1560 gemmho. The last fraction (κ 1560), when redistilled, gave portions of maximum conductivity 1644, 1624, 1600, and 1500, leaving behind a residue of about 10 grams having the disagreeable odour of the higher fatty acids.

Fractional distillation had thus resolved the acid into portions ranging in maximum conductivity from 1500 to over 2000 gemmho, but at no point was there any evidence of a steady value being reached, every portion examined being found to be resolvable even after repeated distillation into fractions of different conductivity.

Purification by Freezing.

Whilst the fractional distillation of the acid was in progress, attempts were made to separate a pure acid by freezing. Two of the intermediate fractions were selected and allowed to crystallise; the mother liquor was poured off from the crystals, and both were diluted to 16 per cent. in order to measure their maximum conductivity. The maximum conductivity values obtained were as follows:

Mixture of fractions from 1625—1650.

Frozen out............	1636
Unfrozen	1636.

Mixture of fractions from 1650—1675.

Frozen out	1652
Unfrozen	1652.

The conductivity of the acid was therefore not affected by fractional freezing, and this method could not be used to prepare a pure acid of definite conductivity. A preliminary freezing is, however, of considerable value in reducing the quantity of impurities to be dealt with by the more efficient methods of purification which are described below.

Purification by Oxidation.

From its behaviour on fractional distillation, it seemed probable that the crude acid might be a mixture of:

	Max. cond.	B. p.
Formic acid	10380	101°
Acetic acid	1640	118
Propionic acid	1113	141
Butyric acid	986	163

and perhaps other acids of higher molecular weight. On account of its high conductivity, formic acid would be by far the most dangerous impurity, and attempts were therefore made to get rid of it by chemical methods. The low-boiling fraction of maximum conductivity 1987 was distilled from potassium dichromate with the idea of removing the formic acid by oxidation, but the distillate still gave the high value 1923, and was evidently far from pure. A second attempt was made to remove the formic acid by distilling from sodium, in the hope that the stronger acid might thus be retained; this method was also a failure, the distillate having a maximum conductivity 1957. Success was finally achieved by the use of potassium permanganate, which reduced the maximum conductivity of a sample from 1753 to 1644 by a single distillation.

Further tests showed that by the use of potassium permanganate an acid of definite properties could be obtained without difficulty from any of the crude commercial samples. In the table which follows, *C* refers to a commercial acid which had been frozen out and drained in order to remove a part of the water, as well as a certain proportion of impurities of high and low boiling points. The acids *A* and *B* were derived from the fractional distillation described above; it should be noted that the original acid was an exceptionally bad sample and had not been subjected to any preliminary purification by freezing; the portions *A* and *B* were almost the extreme fractions, and contained in a concentrated form the impurities of high- and of low-boiling point present in the 10 litres of acid used for the fractionation; they therefore provided a very extreme test of the methods which we have devised for purifying the acid. The course of the purification is shown in the following table:

	A.	*B.*	*C.*
Initial maximum conductivity	1650	1780	1646
Acid distilled from permanganate with 12-pear still-head:			
First portion	1646	1808*	1640
Second portion	1643	1640	1639
Third portion	1628	1638	1640
Fourth portion	—	—	1639

* More permanganate added after this portion had been collected.

Redistilled from a few grams more permanganate:

	A.	B.
First portion	*1638 (60 c.c.)	*1639 (50 c.c.)
Second portion	1637 (1000 c.c.)	1639 (1000 c.c.)
Third portion......................	1638 (1000 c.c.)	1637 (1000 c.c.)
Fourth portion	*1630 (150 c.c.)	*1637 (60 c.c.)

Redistilled from a few crystals of permanganate:

First portion	*1637 (120 c.c.)	1640 (200 c.c.)
Second portion	1641 (1000 c.c.)	1640 (750 c.c.)
Third portion......................	1638 (750 c.c.)	1639 (750 c.c.)
Fourth portion	*1630 (80 c.c. to dryness)	

Again distilled:

First portion	1640 (500 c.c.)	—
Second portion	1640 (500 c.c.)	—
Third portion	1639 (500 c.c.)	—

* Rejected on subsequent distillation.

It will be seen from the above table that a single distillation from permanganate with a 12-pear still-head was sufficient to produce an acid of definite properties, except in the case of a sample in which impurities of higher boiling point had been accumulated deliberately. Even here the quantity of high-boiling impurities was only sufficient to lower the conductivity of the acid by one or two parts in a thousand, but three distillations were required before the final fraction of acid was found to give a normal conductivity maximum. In the case of the acid in which impurities of lower boiling point had been accumulated, the only modification required was to add a rather larger quantity of permanganate in order to secure their complete oxidation.

It should be noticed that the values given above for the maximum conductivity are only relative; the true value of the maximum conductivity is discussed in a later section.

The Freezing Point of Acetic Acid.

The acid, purified as described above, still contains water, which can be removed by freezing and draining. This operation was carried out on a relatively large scale in order to avoid any lowering of the freezing point consequent on the hygroscopic character of the acid. Two Winchester quarts of the purified acid were used, and when sufficiently reduced in bulk were poured into a single bottle and again frozen repeatedly; the quantity remaining for the final determination of the freezing point was not less than 1500 c.c. A device of some value, especially in the later stages of the fractionation, consists in allowing a small lump of the solid acid to remain unmelted as a nucleus for the further freezing of the acid; glaciation then proceeds smoothly over the sides of the

bottle, the thickness of the coating increasing steadily until only a small cone of liquid acid remains in the centre; when the proportion of water is small, the frozen acid is perfectly transparent and compact, and the quantity of water mechanically retained is very much smaller than when freezing is started by shaking the bottle or by introducing a crystal into the cold acid. The freezing point of the liquid acid can be determined at any stage of the freezing by breaking through the crust of acid and lowering a thermometer into the central cone of liquid.

The following table shows the results of successive freezings of the purified acid:

Initial F.P. ...	16·31°	16·45	16·55	16·58	16·59	16·595	16·60
Final F.P.	15·98	16·07	—	16·49	16·49	16·54	16·56

The quantity of acid remaining unfrozen when the "final freezing point" was taken varied from 100 to 200 c.c. in the case of the first five freezings. For the last two freezings the volume of unfrozen acid was only about 20 c.c. from an initial volume of 1500 c.c. In the last freezing the difference between the initial and final freezing points was only 0·04°.

Since each 0·1 per cent. of water lowers the freezing point by 0·2014° (de Visser, *loc. cit.*, p. 118), the amount of water remaining in our acid would be 0·02 per cent. on 20 c.c., or 0·0003 per cent. on the total bulk of 1500 c.c.; the corresponding error in the freezing point would be about 0·0005°. The thermometer used was standardised from one which had been calibrated at the Reichsanstalt, and more recently with very great care at the National Physical Laboratory, the readings of which could be relied on within 0·005°; we consider that our determination of the freezing point of acetic acid is correct within the same limits at 16·60 ± 0·005°.

In this view we are confirmed by the fact that our value is in agreement with the figure 16·5965° ($dt/dp = 0·02435$) given by de Visser (*loc. cit.*) in his investigation of the influence of pressure on freezing point. In these experiments 10 kilos. of acid were frozen fractionally during a period of seven months, until the difference of freezing point between the acid and mother liquor did not exceed 0·0004° when only 1/80 of the acid remained unfrozen. These experiments on the freezing point of acetic acid are obviously by far the most accurate that have been made: the lower values given by almost all other observers are to be attributed to imperfect purification; occasional higher values, for example, 16·7° or 17°, appear to be only rough approximations.

The Boiling Point of Acetic Acid.

The boiling point of the purified acid was determined with the help of a thermometer graduated in tenths of a degree on an open scale from 75° to 125°. The thermometer had been standardised recently at the National Physical Laboratory, the corrections being given to 0·01° at intervals of 5°. In order to reduce the correction for exposed stem, the flask containing the acid was provided with a still-head 40 cm. long, and the thermometer was arranged so that the mercury thread rose only just above the level of the cork. Two hundred c.c. of acid were used, and it was found that three-quarters of this quantity distilled between 118·10° and 118·12° under 768·2 mm. pressure, after applying a correction of $-0·05°$ for thermometer error and $+0·04°$ for exposed stem. The barometer-height reduced to 0° and 45° latitude was 766·0 mm., and the correction to be applied to the boiling point may be taken as 0·038° per mm. (Ramsay and Young, Trans., 1886, **49**, 806, give 0·032°; Schmidt, *Zeitsch. physikal. Chem.*, 1891, **7**, 433, gives 0·043°; Kahlbaum, *Zeitsch. physikal. Chem.*, 1898, **26**, 577, gives 0·038°). The corrected boiling point of the acid may therefore be taken as $118·11° \pm 0·02°$ under 766 mm. (corr.) and $117·88 \pm 0·05°$ under 760 mm. (corr.) pressure. The substantial accuracy of these observations and of the corrections applied in reducing the boiling point is shown by the fact that two preliminary observations under 750 mm. pressure, in which the stem correction was nearly half a degree, gave values for the corrected boiling point which were within 0·02° of that recorded above.

Our value for the boiling point is considerably below those hitherto accepted, practically all of which have been above 118°. In particular it may be noted that Ramsay and Young (*loc. cit.*) give the value 118·5°, Schmidt (*loc. cit.*) gives the value 119·2°, and Kahlbaum (*loc. cit.*) the value 118·6°. The conclusion may therefore be drawn that the last traces of impurity which are removed by the methods we have adopted are substances which have the normal effect of raising the boiling point, as well as lowering the freezing point, of the acid. It should be noticed, however, that the boiling point soon falls below the normal value if the acid is allowed to absorb water; a low boiling point is therefore not a trustworthy indication of the purity of the acid.

The Density of Acetic Acid.

The density of the acid was determined in a double pyknometer of the type recently described by one of us (Bousfield, Trans., 1908, **93**, 679). The figures obtained were:

$$\left.\begin{matrix} d\,18^\circ/4^\circ = 1\cdot05148 \\ d\,20^\circ/4^\circ = 1\cdot04922 \end{matrix}\right\}\text{difference for } 1^\circ = 0\cdot00123.$$

Our experience with this pyknometer justifies us in regarding these results as correct within a single unit in the last figure.

With the help of the temperature-coefficient given above, it is possible to compare our value at 18° with those of other observers, as follows:

	t.	*d.*	*d* 18°/4°.	Diff.
Oudemans (1866)	15°/4°	1·0553	1·0516	+0·0001
Perkin (1884)	15°/15°	1·0568	1·0530	+0·0015
,, ,, ...	15°/15°	1·05704	1·0532	+0·0017
Ramsay (1886)	20°/4°	1·0491	1·0516	+0·0001
de Visser (1893)	16·6°/4°	1·05315	1·05143	−0·00005
Jones (1894)	16·5°/4°	1·0534	1·0516	+0·0001

It will be seen that our value is, as in the case of the freezing point, in very close agreement with that of de Visser; the difference, amounting only to 0·00005, is perhaps due to the increased accuracy which we have secured by the use of a large pyknometer of special design, and not to any difference in the quality of the acid. Three observers using acetic acid purified in the ordinary way have given the density as 1·0516, a value that exceeds ours by one unit in the fourth decimal place, and must be attributed to the same impurities which gave rise to the lower freezing points, 16·4° to 16·5°, recorded by these authors. The chemical methods of purification adopted by Perkin have raised his values for the density by more than 0·001, and must have given an impure product, containing, possibly, appreciable quantities of acetic anhydride.

The Maximum Conductivity of Acetic Acid.

In order to determine the maximum conductivity of the acid, a vessel was calibrated by means of standard solutions of potassium chloride, using the values for the conductivity given by Kohlrausch and Holborn ("Leitvermögen der Elektrolyte," p. 204), namely:

$$\text{KCl } N/50. \quad \kappa_{18} = 0\cdot002397.$$
$$\text{KCl } N/100. \quad \kappa_{18} = 0\cdot001225.$$

These solutions were prepared by diluting to a known volume weighed quantities of a normal solution prepared by dissolving 74·59 grams of potassium chloride to 1044·92 grams of solution, according to the directions given by Kohlrausch, and not according to the more recent values for the equivalent of the salt. The

salt had been crystallised several times from conductivity water until it showed no trace of sodium in the flame test. The water used had a conductivity of $1 \cdot 5 \times 10^{-6}$, which was added to the above values.

The values deduced for the capacity of the vessel were:

$$\text{From KCl } N/50. \quad C = 0 \cdot 2466_1$$
$$\text{From KCl } N/100. \quad C = 0 \cdot 2466_0.$$

This gave for the maximum conductivity of the acid the figure:

$$\kappa_{18} = 0 \cdot 001641_5 + 0 \cdot 0000293\ (t - 18),$$

the temperature-coefficient being deduced from a series of observations in the neighbourhood of 18°.

In determining the maximum conductivity, the Kohlrausch "wheel-bridge" was used, with an alternating current and telephone. The conductivity vessel contained about 40 c.c. Ten c.c. of acid were diluted in a beaker with about 40 c.c. of water from a burette; the conductivity was measured, and the observations were repeated after each of a series of successive dilutions. Thus, in the following series of observations, a minimum bridge-reading and a maximum

Water added	44	46	48	50	51	52	54	57 c.c
Bridge-reading.........	601·9	601·6	601·1	601·0	601·0	601·0	601·1	601·5.

conductivity were reached when 10 c.c. of acetic acid were diluted with 51 c.c. of water; the bridge-reading 601·0, after making the necessary corrections, gives the value for the maximum conductivity set out above.

Practical Methods of Purification.

Having found a method by which acetic acid of the highest degree of purity may be prepared, and having established a reliable value for the maximum conductivity of the acid, it was of interest to determine what amount of purification is needed to produce an acid which can be relied on to give a correct value for this maximum. After testing a number of acids we are able to state that a commercial acid, when purified by freezing and pouring off the liquid portion in order to reduce the amount of water and of oxidisable material, can be relied on to give a correct value if distilled slowly from 2 per cent. of its weight of permanganate, using a 12-pear still-head to retain acids of higher boiling point. In practice the acid can be evaporated to quite a small bulk, but if a standard acid is required it is convenient to reject the first 25 per cent., which contains an excessive proportion of water, and also the last 25 per cent., which may contain homologous acids. The following tests on three of Kahlbaum's acids may be regarded as typical of the observations made.

A. *Kahlbaum's Acid,* "100 *per cent.*"—About one-third of the

acid was melted and poured off; this gave a maximum conductivity 1643 gemmho, and is therefore nearly pure, but cannot be used as a standard without purification.

B. *Kahlbaum's Acid "Free from Higher Homologues."*—The original sample, after pouring away about one-quarter from the partly frozen acid, also gave a maximum conductivity 1643 gemmho. The last 150 c.c. from the distillation of 1500 c.c. of this acid (using a still-head and 1 per cent. of permanganate) gave a normal maximum 1641 gemmho; the whole of the acid could therefore be used as a standard after distillation.

C. *Kahlbaum's Acid*, 99—100 *per cent.*—About one-third was poured away from the partly frozen acid; 2 per cent. of permanganate was added, and the acid was distilled through a 12-pear still-head until only a small residue (containing manganese acetate) was left. The first and last fractions showed a normal conductivity 1641 gemmho, and the whole of the distillate was therefore available for standard acid.

From the above observations, as well as from those quoted earlier in the paper, it is clear that a pure acid can be prepared very readily with the help of potassium permanganate. The original acids usually contain oxidisable material, which raises the maximum conductivity, but this is easily removed by the methods now described. Acids of higher boiling point do not produce any marked error in the maximum conductivity unless (as in our fraction "A") they are present in altogether abnormal quantities; with a 12-pear still-head the acid can be boiled almost to dryness without spoiling the acid for use as a standard of conductivity.

Orton has recently shown that an acetic acid, which is resistant to bromine and which does not give the Adamkiewicz reaction, can be prepared by distilling the commercial acid from phosphoric oxide—one of the two methods used by Perkin in 1884 to purify the acid from moisture. Although this method of treatment is liable to give rise to an acid of lower freezing point and higher density, we have found a normal value, 1642 gemmho, for the maximum conductivity of a specimen kindly sent to us by Professor Orton. We are also indebted to him for the information that a specimen of our acid, which had been prepared in 1902, and might therefore have deteriorated by keeping (it has been suggested that acetic acid oxidises spontaneously to glyoxylic acid), was resistant to bromine, and did not give the Adamkiewicz reaction.

ST. SWITHINS,
HENDON, N.W.

130, HORSEFERRY ROAD,
WESTMINSTER, S.W.

CLXIII.—*Some Oxidation Products of the Hydroxybenzoic Acids. Part III.*

By Arthur George Perkin.

During some experiments with flavellagic acid it was noted that when this substance is heated with sulphuric acid to a high temperature it is converted into a new colouring matter (Proc., 1906, **22**, 114). The investigation of this forms the subject of the present paper.

In a preliminary trial 3·65 grams of flavellagic acid suspended in 30 c.c. of 100 per cent. sulphuric acid were heated rapidly on the sand-bath to 230°, causing the formation of a red-coloured liquid, which effervesced briskly owing to the evolution of sulphur dioxide. The flame was now lowered so that in about half an hour the temperature had fallen to 190°, when the heating was discontinued, the mixture allowed to cool, and poured into a large volume of water. A dull green-coloured precipitate was thus produced, and this was collected, washed, and dried, yielding an almost black, resinous mass, which did not appear to be susceptible of purification by the usual methods. In the finely powdered condition it was therefore added to an excess of hot acetic anhydride containing a little sulphuric acid, and on heating to boiling the dark brown solution gradually deposited a yellow, crystalline powder. This was collected, washed with acetic anhydride, and crystallised from nitrobenzene, from which it separated in pale yellow needles, melting at about 324—329°, and very sparingly soluble in the usual solvents. The yield was 1·2 grams:

Found: C=53·12; H=3·34.

$C_{14}O_{10}(C_2H_3O)_6$ requires C=53·22; H=3·07 per cent.

The acetyl compound suspended in boiling acetic acid was hydrolysed with sulphuric acid in the usual manner, and the product crystallised from pyridine, the only satisfactory solvent for this purpose. An analysis of the substance dried at 160° gave the following result:

Found: C=50·09; H=2·08.

$C_{14}H_6O_{10}$ requires C=50·29; H=1·79 per cent.

The compound consists of small, pale yellow, prismatic needles, which melt above 360°, and are very sparingly soluble in the usual solvents. Concentrated solutions of the alkali hydroxides dissolve it with a greenish-yellow colour, which on dilution become green, and finally of a beautiful blue colour, and these changes

appear to arise from oxidation. If to the substance suspended in water dilute alkali is added drop by drop, the blue coloration is immediately produced, and is of a fairly permanent character. Sodium and potassium carbonate solutions also give blue liquids. As in general properties this new compound closely resembles both ellagic and flavellagic acids, the name *caeruleoellagic acid* is proposed for it. It was now interesting to determine if ellagic acid when heated with sulphuric acid under these conditions reacts in a similar manner, and experiment indicated that this was the case. The crude product thus obtained yielded an acetyl compound, melting at 325—329°, and was identical with acetylcaeruleoellagic acid:

Found: C=53·18; H=3·32.

$C_{14}O_{10}(C_2H_3O)_6$ requires C=53·22; H=3·07 per cent.

An acetyl determination by the indirect method gave 57·24 per cent. of caeruleoellagic acid dried at 160°, whereas the quantity required by the above formula is 57·00 per cent.

The colouring matter thus obtained was analysed with the following result:

Found: C=50·21, 50·01; H=2·44, 2·17.

$C_{14}H_6O_{10}$ requires C=50·29; H=1·79 per cent.

Experiments were now carried out with the object of preparing larger quantities of caeruleoellagic acid, and for this purpose flavellagic acid was employed, as this can be more economically prepared from gallic acid than ellagic acid itself.

The results were at first disappointing, for under the conditions given above and employing mixtures of 20 grams of flavellagic acid in 200 c.c. of sulphuric acid (100 per cent.), it was not easy to control the reaction, and the yield, which in the best circumstances was of a poor character, was thereby considerably diminished. It became evident as the result of numerous trials that caeruleoellagic acid, or possibly the sulphuric ester at first produced, undergoes further change in the presence of sulphuric acid more or less rapidly between 190° and 230°, with formation of a bright yellow compound, and in this case the bright red colour of the acid liquid gradually assumes a dull brown tint. On the other hand, by digesting for a very short time, unattacked flavellagic acid is likely to be present in the final product, the complete elimination of which is exceedingly troublesome. Ultimately it was discovered that the most satisfactory results were obtained by heating the acid mixture to 200°, and at once allowing the temperature to fall to 190°, and remain so for thirty minutes, or by heating to 185° for three-quarters of an hour. The product on pouring into

water was at first dark coloured, but on keeping or boiling the mixture became yellow, suggesting that a sulphuric ester of caeruleoellagic acid or of some accompanying impurity was at first present. Again, if the original red sulphuric acid solution was treated with cold acetic acid a dull red precipitate separated, which in contact with water gradually assumed a yellow tint.

The yield of crude colouring matter, which, when dry, consisted of a dull yellow powder, was, when prepared at the lower temperature, approximately equal to 100 per cent. by weight of the flavellagic acid employed, and from this about 57 per cent. of the pure acetyl derivative could be produced. It was incidentally noted that acetylcaeruleoellagic acid is in reality colourless, and not pale yellow as previously stated, although the latter tint is remarkably persistent and not easily removed. After repeated purification it melted and decomposed at 330—332°, sintering somewhat earlier.

By treatment with fuming sulphuric acid (70 per cent.) at 45—50°, a method which is employed for the preparation of higher hydroxylated compounds in the anthraquinone group of colouring matters, flavellagic acid remains intact, and again it was observed in the high temperature experiments described above that the use of boric acid is not beneficial.

Benzoylcaeruleoellagic acid is prepared by heating caeruleoellagic acid with excess of benzoic anhydride to 220—230° until a clear solution is produced, the reaction being much facilitated by the addition of two or three drops of pyridine, and subsequently at 190—200° for two hours. On cooling to 170—180° and stirring, a semi-solid, crystalline mass is produced, and this sparing solubility of the benzoyl compound in hot benzoic anhydride is characteristic of caeruleoellagic and ellagic acids, and distinguishes these compounds from flavellagic acid, which yields a much more readily soluble benzoyl derivative. To the mixture while still warm a little hot alcohol was added, the colourless powder collected, and purified by recrystallisation from a mixture of nitrobenzene and alcohol. It melted at 343—345°:

Found: C=70·13; H=3·25.

$C_{14}O_{10}(C_7H_5O)_6$ requires C=70·14; H=3·13 per cent.

A benzoyl determination was carried out by suspending the substance (1·15 grams) in a mixture of acetic acid (45 c.c.) and sulphuric acid (14 c.c.), and boiling for about fifteen minutes. The caeruleoellagic acid was collected, and dried at 160°:

Found: $C_{14}H_6O_{10}$=35·28.

$C_{14}O_{10}(C_7H_5O)_6$ requires $C_{14}H_6O_{10}$=34·86 per cent.

Oxidation of Ellagic and Flavellagic Acids with Arsenic Acid.

As caeruleoellagic acid was presumably formed by the introduction of an hydroxyl into flavellagic acid, and of two such groups into ellagic acid, it was sought to determine if the same result would be effected by the oxidation of these colouring matters in sulphuric acid solution with arsenic acid. It is well known, for instance, that under similar conditions alizarin gives purpurin, and other cases could be cited.

Twenty grams of flavellagic acid in 200 c.c. of 96 per cent. sulphuric acid at 100° was treated with 20 grams of arsenic acid, causing the gradual production of a greenish-black precipitate, evidently an arsenic compound of flavellagic acid, in such quantity that the mixture became semi-solid. At the same time, carbon dioxide commenced to be evolved in quantity, and this continued until the precipitate had disappeared, and a rich brown-coloured liquid had been produced. The solution was now heated to 130° for two hours, poured into water, the mixture boiled, the precipitate collected, and repeatedly washed. The product when dry consisted of a brown powder, which weighed 13·5 grams, and was soluble in dilute alkali with a blue coloration. With acetic anhydride and sulphuric acid this gave a colourless, crystalline acetyl derivative (15 grams), but this was evidently a mixture, and attempts to recrystallise it from hot nitrobenzene resulted in the formation of a gelatinous product. Repeated fractional crystallisation, however, from large volumes of acetic anhydride eventually yielded a substance (5·6 grams), which gave crystals with nitrobenzene, and by now employing the latter solvent a product, melting at 329—330°, was eventually isolated. An acetyl determination gave the following result:

Found: $C_{14}H_6O_{10} = 57{\cdot}70$.

$C_{14}O_{10}(C_2H_3O)_6$ requires $C_{14}H_6O_{10} = 57{\cdot}00$ per cent.

Evidently, therefore, this compound consisted of a slightly impure acetylcaeruleoellagic acid, and it was subsequently observed that the complete purification of the colouring matter prepared by this arsenic method can only with certainty be effected by means of the benzoyl derivative. For this purpose the partly purified acetylcaeruleoellagic acid is hydrolysed, and the free colouring matter benzoylated according to the method given above. To the hot semi-solid product a trace of alcohol is added, the crystals collected while the mixture is hot, washed with a concentrated solution of benzoic anhydride in alcohol, and finally with alcohol. By a second treatment in a similar manner, pure benzoylcaeruleoellagic acid

(Found, C=70·05; H=3·26), melting at about 340°, could be isolated.

A benzoyl determination gave $C_{14}H_6O_{10}$=35·53 per cent., and analyses of the free colouring matter (Found, C=50·40; H=1·98) and of its acetyl derivative (Found, C=53·08; H=3·24) showed that there could be no doubt that caeruleoellagic acid is produced when flavellagic acid dissolved in sulphuric acid is oxidised with arsenic acid.

Experiments with the object of improving this process were carried out with disappointing results. Thus it was observed that by employing at 130° larger amounts of arsenic acid the yield of the crude substance was further decreased, although it contained a somewhat larger percentage of caeruleoellagic acid, and again an excess of arsenic acid at 120° for a shorter period gave very little caeruleoellagic acid, but, on the other hand, in this case the oxidation was of a less destructive character.

The mother liquors obtained during the isolation of acetylcaeruleoellagic acid contained a considerable quantity of acetylflavellagic acid, the presence of which was indicated by an acetyl determination (Found, $C_{14}H_6O_9$=60·22 per cent.), and by the fact that with boiling concentrated potassium hydroxide solution it gave hexahydroxydiphenylmethylolid, the acetyl derivative of which melted at 230—233°.

Ellagic acid behaves similarly to flavellagic acid when its solution in sulphuric acid is treated with arsenic acid at 130°. An insoluble arsenic derivative at first separates, a brisk effervescence ensues, and a rich brown liquid is ultimately produced. The crude product of the reaction, which is soluble in dilute alkali with a pure blue colour, is best purified by the fractional crystallisation of the acetyl derivative, and subsequently of the benzoyl compound. An acetyl determination of the former gave $C_{14}H_6O_{10}$=57·23 per cent., whereas the figures obtained by the analysis of the benzoyl compound were C=70·26; H=3·39 per cent.

If a trace of arsenic acid is added to caeruleoellagic acid dissolved in warm sulphuric acid a yellow, curdy precipitate is produced, and this on further heating disappears, with the formation of a deep blue solution. Flavellagic acid behaves similarly, giving a bluish-violet liquid, whereas in the case of ellagic acid the precipitate at first produced merely dissolves with an orange-yellow coloration. When distilled with zinc dust, caeruleoellagic acid yielded a small quantity of oily matter, which on keeping partly solidified. This, after crystallisation from alcohol, formed leaflets having a faint pink coloration, which melted at 111—113°, and evidently consisted of fluorene.

To a boiling mixture of 25 c.c. of water, 25 grams of potassium hydroxide, and 50 c.c. of alcohol, 5 grams of caeruleoellagic acid were added, and the digestion continued until the upper alcoholic layer had distilled off. The product diluted with water was at once poured into acid, the deep brown liquid allowed to remain overnight, and filtered from a small deposit of caeruleoellagic acid which had then separated. The clear liquid was repeatedly extracted with ethyl acetate, the extracts evaporated, and the greyish-white residue crystallised two or three times from water. This compound can also be obtained when aqueous potassium hydroxide is alone employed, but the reaction proceeds better in the presence of alcohol, for air-oxidation is thus almost entirely avoided:

Found: C=51·24; H=3·67.

$C_{12}H_{10}O_8$ requires C=51·06; H=3·54 per cent.

It consists of an almost colourless, crystalline powder, soluble in dilute potassium hydroxide solution with a reddish-violet coloration, which becomes brown on exposure to the air. With ferric chloride it gives a deep brown colour, and with lead acetate solution a nearly colourless precipitate, which quickly develops a bluish-black tint. Nitric acid gives a deep yellow coloration.

The acetyl derivative is prepared by a short digestion of the substance with boiling acetic anhydride containing a trace of pyridine. Addition of alcohol caused the deposition at first of a viscous precipitate; this was removed, and the clear liquid allowed to remain overnight. The crystals which had then separated were purified by recrystallisation from a mixture of alcohol and acetic acid:

Found: C=54·28, 54·31; H=4·60, 4·47.

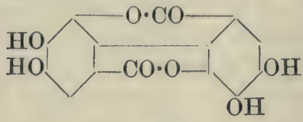
$C_{12}H_2O_8(C_2H_3O)_8$ requires C=54·27; H=4·20 per cent.

It forms colourless needles, melting at 177—178°, and when hydrolysed with a little boiling dilute sulphuric acid deposits the phenol in prismatic needles.

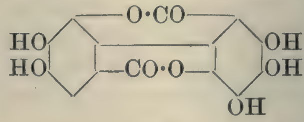
There can be little doubt that this compound, $C_{12}H_{10}O_8$, is in reality an *octahydroxydiphenyl*, and in its general properties it indeed somewhat closely resembles the so-called β- and γ-hexahydroxydiphenyls obtained from ellagic acid by Barth and Goldschmidt (*Ber.*, 1879, **12**, 1244). Although not itself a dyestuff, with iron and aluminium mordanted calico it gives respectively bluish-black and reddish-brown shades, but these colours are evidently due to an oxidation product of the parent substance.

It has been shown by Perkin and Nierenstein (Trans., 1905, **87**, 412) and Perkin (*ibid.*, 1906, **89**, 251) that ellagic acid (I) is the

tetrahydroxy- and flavellagic acid (II) the pentahydroxy-derivative of diphenyldimethylolid:



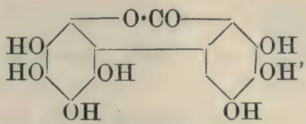
(I.)



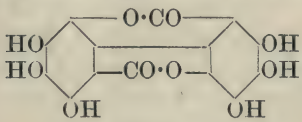
(II.)

and that by means of boiling concentrated potassium hydroxide solution these colouring matters respectively yield pentahydroxy- and hexahydroxy-diphenylmethylolid, although the reaction in the second case proceeds more readily.

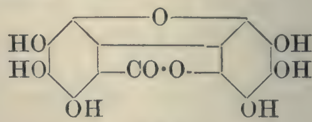
Numerous experiments under varied conditions have failed to produce from caeruleoellagic acid the anticipated heptahydroxy-diphenylmethylolid:



and on this account a doubt at first existed as to whether it in reality possessed the constitution of a dihydroxyellagic acid (III), or might be represented by the formula (IV):



(III.)

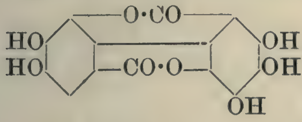


(IV.)

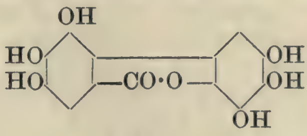
Thus the analytical figures required for both these formulæ and for the corresponding acetyl and benzoyl derivatives show a fairly close agreement, and both compounds constituted in this manner should yield fluorene when distilled with zinc dust. The possibility that caeruleoellagic acid, however, possessed the second of these constitutions was eventually negatived by the production from it of octahydroxydiphenyl.

The ready decomposition of caeruleoellagic acid with alkali in the manner above described is not so difficult to understand when the constitution which has been assigned to it (dihydroxyellagic acid) is considered. The first product of the reaction will consist of octahydroxydiphenyldicarboxylic acid, and it is to be anticipated that this compound, containing as it does both the carboxyl groups in the ortho-position with respect to hydroxyl groups, would in these circumstances readily lose two molecules of carbon dioxide, without the intermediate formation of the monocarboxylic acid corresponding with heptahydroxydiphenylmethylolid. In the case

of flavellagic acid (I) the ease with which this suffers conversion into hexahydroxydiphenylmethylolid (II) is, on the other hand,



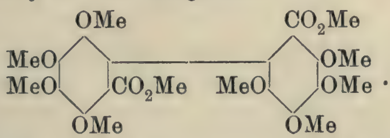
(I.)



(II.)

evident, because the heptahydroxydiphenyldicarboxylic acid produced by means of the alkali contains one of the carboxyl groups in the more stable meta-position.

A further proof of the constitution of caeruleoellagic acid could no doubt be obtained by an investigation of its behaviour when methylated according to the method applied by Herzig and Polak (*Monatsh.*, 1908, **29**, 263) and Herzig and Bronneck (*ibid.*, 1908, **29**, 281) to ellagic and flavellagic acids. In this manner caeruleoellagic acid should yield the compound:



but with the desire of not trespassing on the domain of these authors a study of this reaction was not attempted.

Whereas ellagic and flavellagic acid are obtained when gallic acid is oxidised by means of potassium persulphate and sulphuric acid (*loc. cit.*), it suggested itself that by working at a higher temperature and employing an excess of the reagent, caeruleoellagic acid might be prepared by this method. An experiment indicated that such is probably the case, for the crude product of the reaction dissolved in dilute alkaline solutions with a somewhat bluer tint than that given in these circumstances by flavellagic acid itself. The main bulk of the substance was, however, flavellagic acid, and it was not found possible by a use of the methods described above to isolate the very small quantity of caeruleoellagic acid which appears to be present in the mixture.*

Caeruleoellagic acid possesses well-marked dyeing properties of a similar character, although more strongly developed than those of ellagic and flavellagic acids, and may have practical utility. Owing to its sparing solubility, it gives the best results in the paste form, for which purpose it is preferably dissolved in hot sulphuric acid,

* Experiments with the object of introducing further hydroxyl groups into catellagic acid, the dihydroxydiphenyldimethylolid derived from protocatechuic acid by means of arsenic and sulphuric acids, or by the action of sulphuric acid at high temperatures, have given negative results.

precipitated by water, and thoroughly washed. The following results were obtained by employing mordanted woollen cloth.

Chromium.	Aluminium.	Tin.	Iron.
Deep olive-yellow.	Greenish-yellow.	Dull yellow.	Greenish-black.

In the case of the aluminium mordant the employment of chalk in the dye-bath exerts a detrimental effect.

By the inclusion of Herzig and Tscherne's resoflavin (*Annalen*, 1907, **351**, 24), prepared by the oxidation of 3:5-dihydroxybenzoic acid, a series of hydroxydiphenyldimethylolid derivatives is now known to exist:

Metellagic acid, $C_{14}H_5O_4(OH)$.
Catellagic acid, $C_{14}H_4O_4(OH)_2$.
Resoflavin, $C_{14}H_3O_4(OH)_3$.
Ellagic acid, $C_{14}H_2O_4(OH)_4$.
Flavellagic acid, $C_{14}HO_4(OH)_5$.
Caeruleoellagic acid, $C_{14}O_4(OH)_6$.

CLOTHWORKERS RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS.

CLXIV.—*The Interaction of Formic Acid and Cellulose.*

By CHARLES FREDERICK CROSS and EDWARD JOHN BEVAN.

PRODUCTS of interaction of cellulose and formic acid have been described in various communications (Berl and Smith, *Ber.*, 1907, **40**, 906; R. C. Woodbridge, *J. Amer. Chem. Soc.*, 1909, **31**, 1067) and patent specifications, and it is generally assumed that such products are formed by a process of simple esterification. The probability of formic acid reacting in more than one way should, however, be taken into account, and also, as a factor in the reaction, the labile equilibrium of the cellulose complex and its tendency to change its configuration under the action of reagents (Trans., 1904, **85**, 691).

The possible modes of action of formic acid are in addition to the normal replacement of alcoholic hydroxyl groups by the O·COH residue: (1) As a consequence of the avidity of the acid, an attack on the cellulose complex by hydrolysis or condensation, or by both processes concurrently. (2) The acid may react through its carbonyl oxygen atom, and give rise to complexes, thus:

$$\begin{matrix}H\\HO\end{matrix}\!\!>\!CO + \begin{matrix}H\cdot X\\H\cdot Y\end{matrix} = H_2O + \begin{matrix}H\\HO\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}X\\Y\end{matrix}.$$

As regards the cellulose we cannot pretend to predict the course of change or the final equilibrium under (1); and under (2), if reaction takes place, it suggests the existence in cellulose of pre-formation according to (1) of $CH_2\cdot CO$ groupings. This is an

hypothesis justified by well known transformations of the carbohydrates (as in the production of levulic acid from the hexoses), and more particularly of cellulose under the action of acids.

These considerations have been formulated as the result of an investigation of typical derivatives of this group manufactured by processes already worked on the industrial scale. These compounds are found to be divergent in properties and general characteristics from what might be accepted as the normal, defined from analogy to the better known esters, and especially the acetates.

Experimental.

The products which we have more particularly studied were prepared and supplied to us by Professor Dr. E. Bronnert (Mulhouse), and were (*a*) a voluminous, white solid, and (*b*) a transparent film, (*a*) being the direct product of interaction of formic acid and cellulose (without catalyst), and (*b*) being obtained by spreading a solution of (*a*) on a glass surface, and evaporating the solvent acid.

Examination of (*a*):—The product was soluble in pyridine and nitrobenzene; a characteristic solvent was found in the alkali thiocyanates (for example, of potassium and ammonium); a 20 per cent. solution of these salts dissolved the compound freely.

When dried in the air the substance contained 8—9 per cent. of water.

After swelling with pyridine, the action of $N/2$-aqueous-alcoholic sodium hydroxide was rapid:

Found: Acid (as CH_2O_2) = 44·0. Residue (cellulose) = 76·6.

Cellulose diformate requires Acid (as CH_2O_2) = 43·2; Residue (cellulose) = 74·3 per cent.

Under the direct action of the $N/2$-alkali, the saponification is less rapid, and higher acid numbers are obtained (CH_2O_2 = 46 per cent.) as a result of long-continued action.

On analysis of the anhydrous compound the following numbers were obtained:

0·1498 gave 0·2425 CO_2 and 0·0712 H_2O. C = 44·15; H = 5·38.

$C_7H_{10}O_6$ (monoformate) requires C = 44·2; H = 5·26 per cent.

These numbers do not correspond with the composition represented by the results of saponification. In other elementary analyses there was a still closer approximation to the numbers for cellulose, and therefore further divergence from the theoretical numbers for a diformate, which requires C = 44·0; H = 4·58 per cent. These variations were probably due to the fact that the compound proved to be unstable.

After being kept for four months (in a closed bottle) it was no

longer soluble in pyridine, and was found to have developed acidity; it contained free acid (calculated as CH_2O_2) equal to 10·0 per cent. of its weight. After removing this free acid, the compound was boiled with water. Further volatile acid distilled over, which amounted to 10·8 per cent., a total of 20·8; the loss of formic acid (1 mol.) from a diformate should be 21·1 per cent. As an explanation of these results we may assume that the original compound is a monoformate, but of a modified cellulose complex, the second molecule of formic acid, obtained on saponification, being a product of decomposition of this complex, and this is confirmed by the following experiments.

Acetylation:—The compound was mixed with 10 parts of acetic anhydride at 50°, and a 15 per cent. solution of zinc chloride in glacial acetic acid was added; the substance dissolved completely. The solution was boiled in one experiment for one hour, and in a second for five minutes, and the new ester precipitated by pouring into water.

The yield in both cases was the same, namely, 120 per cent., and corresponds with the subjoined numbers defining the composition of the product. On analysis:

0·1725 gave 0·3301 CO_2 and 0·0769 H_2O. C = 47·48; H = 4·96.

$C_{11}H_{14}O_8$ (a diaceto-monoformate) requires C = 48·18; H = 4·75 per cent.

This diaceto-monoformate neutralised 46 per cent. of its weight of sodium hydroxide, and gave an insoluble residue (cellulose) = 54·5. ($C_{11}H_{14}O_8$ requires NaOH = 46; cellulose = 59·1 per cent.) The amount of cellulose found was as usual low, owing to unavoidable further hydrolysis. When dried in the air the compound retained 1·5 to 2·0 per cent. of moisture, which is within the normal low limits characteristic of the true esters.

The instability of the original ester is thus also shown on acetylation, as one formyl group is displaced when two acetyl groups enter the molecule.

There is, however, further evidence as to the constitution of the original ester, confirming the view that in the reaction by which it is produced the cellulose complex undergoes constitutional modification.

(1) A careful examination of the acid products of saponification, using aqueous sodium hydroxide only, showed that acetic acid is produced. The acid was separated by fully oxidising with permanganate the volatile acids first obtained, redistilling, and finally crystallising the silver salt. (Found: Ag = 64·85. Calc., Ag = 64·65 per cent.)

The acetic acid thus formed must be a product of resolution of the new cellulose complex.

(2) The cellulose residue showed divergencies from the normal; thus, on analysis:

0·1300 gave 0·2133 CO_2 and 0·0810 H_2O. C=44·60; H=6·93.

The value for hydrogen is an indication of the production of methyl groups, involving, therefore, the migration of hydroxyl groups within the cellulose complex.

This "cellulose" was acetylated, and gave a high yield (185 per cent.) with an exceptionally high acid number on saponification [acid (as $C_2H_4O_2$)=81·1] and correspondingly low cellulose residue (27·3). These numbers and relations are sufficient to indicate the more complex nature of the interaction of cellulose and formic acid (*supra*). Further investigation is required for the full elucidation of the constitutional modification which cellulose appears to undergo.

Examination of (*b*):—This was a transparent uniform film of 0·085 mm. thickness. From the dimensions we were able to estimate closely the volume of a given weight, the specific gravity being found to be 1·520; that is, in the normal air-dry state. The moisture retained in this condition was 13·0—16·0 per cent. Both figures are widely divergent from those generally characteristic of the cellulose esters. The film was found to resist the general solvents of these esters, as well as the special solvents noted for the product (*a*). Analysis gave:

Anhydrous substance:

0·1281 gave 0·2052 CO_2 and 0·0744 H_2O. C=43·7; H=6·4.
0·1454 ,, 0·2355 CO_2 ,, 0·0812 H_2O. C=44·1; H=6·2.

$C_6H_{10}O_5$ requires C=44·4; H=6·1 per cent.

Air-dried substance:

0·1579 gave 0·2224 CO_2 and 0·0988 H_2O. C=38·4; H=6·8.

$C_6H_{10}O_5+H_2O$ (15·8 per cent.) requires C=38·39; H=6·85 per cent.

So far, therefore, there is nothing to identify this product as an ester; it has the composition and properties of a cellulose.

Saponification of the substance with $N/2$-aqueous-alcoholic sodium hydroxide proceeded with some difficulty. The following results were obtained:

Duration of boiling.	Acid formed, calc. as CH_2O_2.
9 hours	25·0
Further 6 ,,	12·1
,, 4 ,,	4·4
	41·5

These results indicate a course of action different from the saponification of an ester: rather a progressive decomposition of a cellulose complex with production of acid groups.

With the view of elucidating this point, we carried out some experiments on the interaction of formic acid and typical celluloses.

(*a*) Cotton, wood, and esparto celluloses were taken as types of the generally accepted classification. The action in these cases is slow, and accompanied by considerable discoloration (brown). Products of condensation are formed. The fibres gelatinise, showing progressive hydration, and the action differs markedly from that of other acids comparable in general functions with formic acid.

On treating with water and washing, we obtained:

Percentage of original.	Cotton.	Wood cellulose.	Esparto.
Insoluble product	99·0	91·0	82·5
In solution	5·7	11·4	—
Total	104·7	102·4	
Saponification of insoluble product: yield of acid as CH_2O_2	18·11	22·45	26·2

It is to be noticed that with a small gain of weight due to the fixation of the formyl residue, there is a relatively large production of acid on saponification. In other words, the celluloses are constitutionally modified, and, as a result, are decomposed by alkalis with the formation of acid products.

(*b*) Cellulose (hydrate) regenerated from solution as xanthate (viscose).

On digestion at 60° there is a very gradual attack, the cellulose passing into a viscous solution. On dilution, the product is precipitated. The following determinations were made:

(1) Twelve hours' digestion—incomplete solution.

(2) Twenty-four hours' digestion—nearly complete solution.

	(1.)	(2.)
Reprecipitated	89·4	85·42
Products in solution: (Residue on evaporation)	20·4	35·80
	109·8	121·22

The insoluble product from (2) on saponification showed acidity equal to 44·00 (calc. as CH_2O_2). These numbers and incidental observations lead to the conclusion that this form of cellulose (hydrate) is attacked without formation of condensed coloured products. There is no discoloration, even on raising the temperatures to 100°, and the viscosity persists when the heating is long continued; at the same time a portion of the cellulose is degraded to soluble products of low molecular weight. These products were acid in higher proportion. We have also made a *comparative* study of the interaction of formic acid (99 per cent.) and the hydrated celluloses obtained from solutions in cuprammonium, and as xanthic ester (viscose). These show similar behaviour. With the acid alone, prolonged digestion at temperatures up to 45° failed to effect more than partial solution (30 per cent.). The presence of catalysts effects a marked change. With 20 parts

of the acid containing 2 per cent. of zinc chloride in solution, a homogeneous product was obtained in twenty hours' digestion at 45°. The purified product was analysed:

0·1713 gave 0·2758 CO_2 and 0·0716 H_2O. C=43·91; H=4·65.

A diformate requires C=44·0; H=4·58 per cent.

With phosphoric acid the action is especially rapid. In a typical case, we obtained a yield of 116 per cent. of the insoluble product, which on saponification gave, acid (as CH_2O_2)=49·5 and residue (cellulose)=56·4 per cent.

Owing to the difficulties inherent in investigations of cellulose products it will be necessary to extend these observations to other polyhydroxy-compounds of which the products of possible decomposition are better known, or which, from simplicity of molecular structure, can be studied in relation to synthetic reaction with greater precision of data.

In one direction we have examined starch, which shows many analogies to cellulose in its reaction with formic acid; products insoluble in water are obtained, and these also, on saponification, show acidity in excess of the molecular proportions of acid actually combining. We have also studied certain aromatic compounds under similar conditions of interaction, and although there is no direct relationship of these to cellulose, it is well known that, through the lignocelluloses, there are many suggestions of a cyclic constitution of cellulose.

The following is a brief account of the results obtained with typical aromatic hydroxy-compounds.

Resorcinol reacts with formic acid, and in the presence of hydrochloric acid the change is rapid, a substance being formed with considerable development of colour (crimson). The main product is easily isolated by crystallisation from water:

0·1482 gave 0·3397 CO_2 and 0·0714 H_2O. C=62·5; H=5·3.

$C_{13}H_{12}O_5$ requires C=62·9; H=4·8 per cent.

The formula suggests that the compound is a *dihydroxybenzhydrol*, formed according to the equation:

$$2C_6H_6O_2 + CH_2O_2 = HO{\cdot}CH[C_6H_3(OH)_2]_2 + H_2O.$$

The alkaline solutions of this substance are very strongly coloured (crimson). The *penta-acetyl* derivative was recrystallised from alcohol:

0·250 gave $C_2H_4O_2$=67·2.

$C_{23}H_{22}O_{10}$ requires $C_2H_4O_2$=65·5 per cent.

Quinol gives no reaction under similar conditions, and it appears, therefore, that condensation takes place in the para-position with respect to a hydroxyl group. This is confirmed by experiments on α- and β-naphthol. The latter does not react with formic acid, whilst the former gives a small amount of a condensation product,

which is insoluble in water, but reacts with alkalis, giving grass-green solutions. The reaction of the naphthols with acetaldehyde are analogously divergent (Claisen, *Ber.*, 1886, **19**, 3316).

Phloroglucinol reacts rapidly, but the first product appears to be phloroglucide (Found, C=61·3; H=4·0. Calc., C=61·4; H=4·2 per cent.), which would be formed according to the equation:

$$2C_6H_6O_3 = C_{12}H_{10}O_5 + H_2O.$$

With resorcinol and phloroglucinol in molecular proportions, we obtained intermediate results; the main product after crystallisation was analysed:

0·1360 gave 0·3229 CO_2 and 0·0468 H_2O. C=64·7; H=3·8.

$C_{13}H_{10}O_5$ requires C=63·4; H=4·0 per cent.

This compound is probably formed according to the equation:

$$C_6H_6O_2 + C_6H_6O_3 + CH_2O_2 = C_{13}H_{10}O_5 + 2H_2O.$$

To connect these observations with cellulose it is only necessary to remember that the CH . . . OH(1:4) grouping of a phenol alternates with, and, in fact, reacts as, the grouping CH_2 . . . CO, and a keten grouping has been shown by ourselves to be definitely characteristic of the lignocelluloses and inferentially of the celluloses ("Cellulose," 1895, and "Researches on Cellulose," I. and II., 1900–1905). Collie has developed the potentialities of the keten and multiple keten group from a broader point of view, and applies his conclusion to the carbohydrates, including cellulose (Trans., 1907, **91**, 1806).

From the results so far obtained we may conclude that the formyl derivatives of cellulose are not the analogues of the acetates, the reactions of formation certainly introducing other factors which we have indicated, and our further investigations will have reference to the influence of these, as a working hypothesis.

Incidentally, these results suggest a clue to anomalies, and the apparently contradictory results of investigators in regard to the acetates of cellulose (Berl and Smith, *loc. cit.*; Ost, *Zeitsch. angew. Chem.*, 1906, **19**, 993; J. Gutsche, *Diss.*, Göttingen, 1910), which we shall discuss in a subsequent communication.

We are indebted to Professor Bronnert for the supply of products as stated, and we have pleasure in acknowledging experimental results included in this paper from Mr. S. S. Napper, and our indebtedness to Messrs. S. Courtauld and Co. for their valuable collaboration. We wish also to mention the efficient services of our assistant, Mr. D. R. Davey, throughout these investigations.

4, New Court,
London, W.C.

OBITUARY NOTICE.

JAMES CAMPBELL BROWN.

BORN JANUARY 31ST, 1843; DIED MARCH 14TH, 1910.

JAMES CAMPBELL BROWN was born at Aberdeen on the 31st of January, 1843. His father was Mr. George Brown, of Messrs. G. Brown and Co., Alum Works, Bow Common, London. He came of an old Scottish family, connected by marriage with the Grahams, Dukes of Montrose and the Earls of Strathmore. As a boy he attended the Gymnasium in Old Aberdeen, a famous school in its day, by reason of the character and attainments of its head, Dr. Alexander Anderson. In 1857 he entered Marischal College in Aberdeen, and attended the classes there in Latin and Greek; subsequently he passed through the classes of the first two years of the medical curriculum, specially distinguishing himself in botany and chemistry. Originally he had intended to take up medicine as a profession, but his interest in science had been aroused, and in 1863 he proceeded to London to study under Tyndall and Hofmann at the Royal College of Chemistry, and also at the School of Mines. He matriculated in 1862 at the London University, obtained the degree of Bachelor of Science in 1867, with first class honours in chemistry, and the degree of Doctor of Science in 1870. In 1907 the University of Aberdeen conferred on him an honorary degree of LL.D. His career as a teacher began in 1864, when he was appointed assistant to the Professor of Chemistry at Aberdeen University. In 1867 he was appointed lecturer in Experimental Science and Toxicology at the Liverpool Royal Infirmary School of Medicine. Henceforward to the end of his life he was associated with Liverpool. In 1872 he married Ellen Fullerton (daughter of John Henderson, of Quarry Lodge, Aberdeenshire), who survives him.

During the whole forty-three years he was connected with Liverpool he was keenly interested in education; and the present generation of teachers in the North are perhaps not fully aware how much they owe to Professor Campbell Brown. In 1877, ten years after he came to Liverpool, he had become Chairman of the Royal Infirmary School of Medicine. It was at this period that he and the late Mr. W. J. Stewart, stipendiary magistrate of Liverpool, were elected joint-secretaries of the committee for organising a University College in Liverpool; the amount of work done in con-

nexion with this committee must have been very great, and as an organiser Dr. Campbell Brown came prominently to the fore.

When the School of Medicine was merged in the newly-formed College, two Chairs were founded to take the place of the lectureship in Experimental Science. The Chair of Physics was occupied by Professor Lodge (now Sir Oliver Lodge), and the Grant Chair of Chemistry by Professor Campbell Brown. Henceforward, he never spared himself in efforts that might benefit the development of his department or the training of students. His heart was bound up in the success of the chemical school, and to the time of his death improvements and additions were being made in the laboratories.

There are many men who are proud to have studied under him, and there are many more who owe to him their first start in life, for he took immense trouble in finding suitable posts for his students when they had to leave the College. He was in intimate touch with the chemical manufacturers of Lancashire and Cheshire, and was able to supply them with well-trained men.

In 1884 the chemical laboratories at University College, Liverpool, were built, and further extensions were made by 1886. In the session 1896–7 the William Gossage Laboratory was opened, and rooms were added for metallurgy, electro-chemistry, and gas analysis. Recognising that electro-chemistry was a subject of great importance in University training, Professor Campbell Brown obtained the help necessary for the founding of a lectureship in that subject, and soon afterwards, by the help of Mr. Muspratt and Sir J. Brunner, the Muspratt laboratories were built.

Besides being connected with the University College of Liverpool, Professor Campbell Brown was a public analyst as well, and his services to the community in suppressing the adulteration of food were of the greatest value. In 1872 he was appointed public analyst to the city of Liverpool, in 1873 he was also appointed to the same post for Cheshire and the Isle of Man, and in 1875 for Lancashire. The latter position he retained till his death. He was an original member of the Society of Chemical Industry, and also of the Society of Public Analysts. He was elected a Fellow of this Society in 1867, and was one of our Vice-Presidents when he died on March 14, 1910.

Professor Campbell Brown was always an enthusiastic advocate for investigation and research, and there were very few years during the period 1870–1910 in which he published nothing. His earliest paper in 1870 was on "The artificial formation of organic compounds," and his last was published after his death in the Proceedings of the Chemical Society, the title being: "An appara-

tus for the distillation of fats and fatty acids in the vacuum of the cathode light."

The ground covered in his original communications was very wide; pure and applied chemistry, analytical, toxicological, and botanical subjects are all represented. Perhaps his principal contribution to applied chemistry, at least the one that was of immediate and great practical value, was a report published in 1874 on the agricultural chemistry of the plantations of India. This was the outcome of a long series of analyses of healthy and unhealthy tea plants, and of the soils in which the tea plant was growing. The result of this work was the devising of a fertiliser for use in the plantations, which proved remarkably successful, but he never took any steps to secure for himself a pecuniary interest in the extensive use to which this fertiliser was put.

The bulk of his earlier publications were on analytical subjects; analysis of butter, pepper, and other substances; and his experience in this branch of chemistry was very large indeed. He was always trying in every way to suppress the adulteration of food. In the early days, when he was appointed public analyst for Liverpool under the Adulteration of Foods Act, this was no easy task. It was he who had to plan and superintend the building of the chemical laboratories, and organise routine methods for the analysis of foods and drugs on the large scale.

He was always ready to do all in his power for the purpose of raising the profession of the public analyst, and he recognised that the most important factor in an analyst's work was accuracy. In his own analytical laboratories his method was always to have every analysis repeated in its essential portion by a second operator, and, when possible, by a different method, thus as far as possible avoiding error. His zeal for "precise" methods and his dissatisfaction with all others was one of his most characteristic points.

He was also appointed analyst to the Water Committee of the City of Liverpool, and to all the local authorities in the administrative county of Lancaster. He was frequently consulted in reference to large schemes of public water supply, such as Hawes Water, the Vyrnwy watershed, the Liverpool supply, the new Birmingham supply, the Birkenhead supply, and others. His experience in this subject is, in part, embodied in various papers, for one of which, "Deposits in pipes and other channels carrying potable waters," he was awarded, in 1904, the "Manby Premium" by the Council of the Institute of Civil Engineers. As a toxicologist, he had a large experience, especially in cases connected with arsenic poisoning.

Apart from chemistry, Professor Campbell Brown was a many-

sided man, a distinguished botanist, a lover of music and literature, and a great lover of nature.

At his property at Wedderhill, near to Stonehaven, he made a wonderful Alpine garden, full of every kind of Alpine plant, which was an endless source of enjoyment to him in after years. To those who knew him well, Professor Campbell Brown was a man of whom it is particularly hard to have to say "We shall see him no more." Honest, sturdy, straightforward, kindly, and with a keen sense of humour, he went through life doing good to everyone.

As a teacher and organiser, the University of Liverpool owes him a deep debt of gratitude. The chemical world has lost a member who, in all his scientific work, always set before himself the ideal that if a thing was worth while doing, it was worth while doing well.

At the close of a long life, to his honour be it said, he was still engaged in research, in most important public duties, and in ensuring that his students began their lives as well-trained and competent chemists.

H. B. D. and J. N. C.

CLXV.—*A Method for the Accurate Volumetric Determination of the Oxygen in Air.*

By HERBERT EDMESTON WATSON (1851 Exhibition Scholar, University College, London).

PROFESSOR P. A. GUYE and the author have recently ascertained that if the atmosphere were calm there would be a considerable reduction in the percentage of oxygen at high altitudes. If the quantity is taken as 21·00 per cent. at the surface, the amount at 1000 m. altitude is only 20·73 per cent. Owing, however, to the presence of winds, it seems very unlikely that there is in reality any detectable difference, unless, as is not impossible, the upper layers of the atmosphere constitute a region of absolute calm.

Sufficient data to throw light on this question are not yet available, and it is with a view to carrying out a large number of analyses of air collected systematically at different altitudes that the apparatus now described has been designed. For this purpose it is necessary to make use of a method which is as accurate as

possible, but at the same time the question of rapidity is also of considerable importance.

In practice, the estimation of the oxygen in air is carried out by removing this element in some suitable way, and determining the amount of residue. Absorption by heated copper, as performed by Dumas and Boussingault (*Ann. Chim. Phys.*, 1841, [iii], **3**, 257), involves complicated apparatus, and is slow. The gravimetric method of Leduc (*Compt. rend.*, 1896, **123**, 805), in which the oxygen is absorbed by cold phosphorus contained in a closed bulb, is apparently very accurate, but requires twenty-four hours for the absorption to take place, and also involves the weighing of large glass bulbs, an operation which should be avoided if possible.

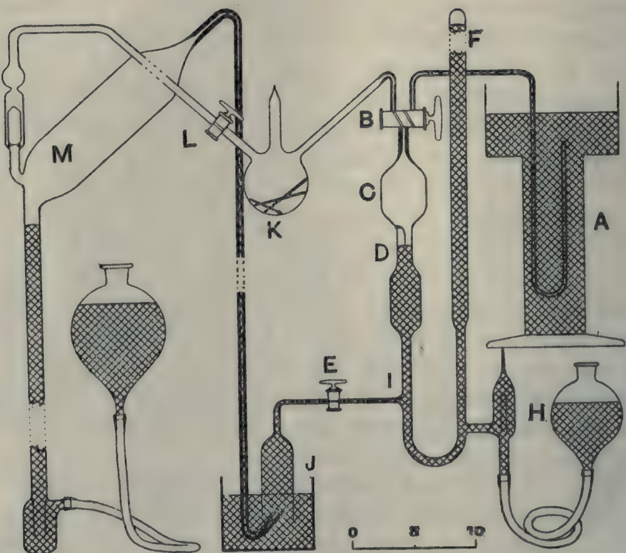
The volumetric method used by Regnault for an exceedingly large number of analyses (*Ann. Chim. Phys.*, 1849, [iii], **26**, 329; and 1852, **36**, 385) was very simple and rapid, but had several disadvantages. The air was mixed with hydrogen, and exploded, the volume being kept constant, and pressure changes noted. To avoid drying the gas, the measuring tube was always kept moistened with water, thereby probably causing a slight variation in volume. Regnault also applied no compressibility correction, although the error from this cause is very small. In addition, it had been recognised as early as 1836 by De Saussure (*Mem. Soc. de Phys. et d'Hist. Nat. Genèvè*, 1836, **7**, 447) that ammonia was produced by such explosions of hydrogen and air, and to avoid this he devised the elegant, although tedious, method of shaking the air with lead shot and water in a closed bottle, and weighing the amount of water which entered when absorption was complete and the bottle was opened under water.

It is hoped that by means of the present apparatus some of the above-mentioned difficulties may have been eliminated. The general arrangement is shown in the annexed diagram, and it should be noted that special attention is given in the construction to the volumes of the various constituent parts, as this considerably facilitates the subsequent manipulation. Several small details are also important, and will be mentioned as they occur. The construction of the apparatus and the method of using it is best explained by following through the operations carried out in a complete analysis.

The air is introduced into test-tubes with a volume of just over 50 c.c., on the top of which some potassium hydroxide has previously been fused. These are inverted over mercury, and the gas allowed to remain in them at least two hours before analysis in order to remove carbon dioxide and water vapour.

The gas is admitted through the inverted syphon *A* and the

two-way tap B to the burette C, but a small quantity of gas must be left behind in the syphon to avoid filling the tube between B and C with mercury. The height of the mercury is then adjusted by means of the reservoir H until it just touches a point D, which is set in the middle of a piece of the same tubing as that from which the manometer tube F is constructed, both being about 1 cm. in diameter. F may be either evacuated, boiled out, and sealed off, or, better, connected to a small pump in which a good vacuum is maintained. The difference of level of the mercury in F and at D is then read with a cathetometer as well as the meniscus heights in case their difference is sufficient to require the application of a



correction to the pressure. The whole of the burette and the manometer tube is enclosed in a water-jacket (not shown in the diagram) of considerable dimensions, the water being at room temperature. Unless the external temperature is changing very rapidly, it is a matter of no difficulty to maintain the temperature of the water at C constant to 1/50 of a degree for some time previous to, and during, the measurements.

The bulb K, carefully made of thin glass and 60 c.c. in volume, contains about 5 grams of yellow phosphorus. This is introduced before a series of experiments through the tube at the top of the bulb, which is then sealed off, and the bulb evacuated by means of the small Antropoff pump M (compare *Chem. Zeit.*, 1910, **34**,

979) with a delivery tube not exceeding 0·75 mm. in diameter. After measurement, the air is admitted into K (the tap L being closed), and the mercury in C passed well beyond the tap B, which is then turned off. K is next heated with a smoky flame for about five minutes, a procedure which appears to absorb the oxygen completely.

After allowing about twenty minutes for the vapours to settle, B is opened and H lowered until the mercury falls just below the T-join I, and half the gas passes back into the burette. B is then closed, and the remaining gas pumped into J. The volume of J being 20 c.c., the gas completely fills it, and no bubbles can stick to the sides. The delivery tube of the pump must, however, always be tapped when all the gas has been pumped off, because a bubble invariably remains on the end unless this is done. The tap E is next opened, and the gas from J passes into the burette. The total volume of the latter is 60 c.c., so that the pressure inside after the admission of the gas is sufficiently low to cause the mercury to rise in J and pass to I. The capillary tube between these two points is of 0·5 mm. bore, and very carefully blown on at each end so as to form no hollow in which a bubble of air could catch. It is also necessary to turn the tap right round once or twice to make sure that no bubble remains in the bore. While the mercury is running in from I, the reservoir H is carefully raised, and it can at once be seen if any air remains at I, and, if so, it is quite easy to displace it by again lowering H.

The mercury is then again raised to the point D, and after a short interval the pressure and temperature are measured, and the gas expelled from the apparatus through A.

Allowing fifteen minutes to elapse before taking each pressure reading, twenty minutes for the phosphorus vapours to settle and grow cool, and fifteen minutes for complete evacuation with the pump, the whole analysis may easily be performed in an hour and a-half.

More phosphorus may be introduced from time to time as considered necessary. It is not easy to say for how many analyses a given quantity of phosphorus will suffice, but on one occasion when 2 grams had been used for about ten analyses, it was found that only a small fraction of the whole had been oxidised or converted into the red variety. At intervals the whole bulb K may be cut down and cleaned. It should be noticed that the oxides of phosphorus in this bulb form the only drying agent in the apparatus. Since the gas is introduced dry, even this is unnecessary, but it is absolutely essential before starting work for the first time to circulate the dry nitrogen formed in the first combustion through all parts of the apparatus at least three or four times.

The calculation of the results is simple. Since 50 c.c. of air are used for the analysis, it will be seen that after absorption of the oxygen, and when the gas is being again measured, the pressure in the burette is approximately atmospheric, whilst, in addition, the bore of the tap B leading to K is filled with gas at half this pressure. Any error due to this cause, however, even with a tap of large bore, is automatically eliminated, for it will be observed that this gas remains in the apparatus when the rest is expelled at the end of the experiment. On introducing another sample of air, the volume is measured between the barrel of the tap and the point D. The gas remaining in the tap bore from the previous experiment is added to this air when it is admitted to K, but an equal volume is again retained in the tap bore at the end of the experiment (assuming, of course, that approximately equal quantities of air are used for each analysis), so that the volume between the barrel of the tap and the point is the true volume of the nitrogen in the added air. It is hardly necessary to add that this tap must be greased as lightly as possible.

Consequently, if p be the pressure of the air, T its absolute temperature, and $p'T'$ the corresponding quantities for the gases remaining after absorption, the percentage of these gases is given by $100p'T/pT'$.

It may be remarked that, assuming T constant, if p is one atmosphere, p' is the partial pressure of the residual gases, thereby measuring the proportion in which they occur, or, dealing with volume, p'/p gives the ratio of the volume of the residual gases measured at their true partial pressure (and corrected to atmospheric pressure, assuming Boyle's law to be true) to the total volume. This is the only rational method of stating results given as percentages, for in any other case, if, for instance, the oxygen and residual gases were both measured separately at atmospheric pressure, the sum of the two separate volumes would not be equal to the volume when mixed. Actually, in these experiments it is better to measure the air under increased pressure and the residues under atmospheric pressure in order to make the barometer readings rather more accurate, but the change in the value of p'/p when this is done is less than 1 part in 50,000, and consequently negligible.

With regard to the accuracy of the method, in each of the two sets of measurements there are two manometer readings and a temperature determination. The error in each of the former should not exceed 1/20 mm., that is to say, 1 part in 15,000, and the temperature should be correct to 0·02°, or 1 part in 15,000. If this be so, the total maximum error in the final result due to these causes is 6 parts in 15,000, although if the apparatus is rigidly

fixed the errors in reading to the fixed point should be less than that given. The chance of this maximum deviation occurring is, moreover, only 1 in 32.

Assuming that a mercury surface can be set to a point with an accuracy of 0·02 mm., the error in volume thus introduced is about 1 in 25,000 for a tube of the size used. It may, however, be necessary to apply a small correction if the height of the meniscus does not remain constant. If the burette is of fairly thick glass, the change of volume with pressure is negligible.

There are two other possible sources of error. First, a bubble of air may adhere to the glass somewhere. If, however, the experiments are carried out as described, this will not be found to occur, and as, moreover, 1 cu. mm. of air can readily be seen, corresponding with 1/14,000 of the whole volume, no error should arise from this cause. Secondly, there is the possibility of incomplete absorption by phosphorus. There seems, however, to be every reason to suppose that even if traces of oxygen do remain, the quantities are too small to detect or measure, except by electrical methods. Leduc (*loc. cit.*) could detect no error in his experiments, owing either to insufficient absorption or to the vapour pressure of the phosphorus, and in the present series no variation which could be ascribed to these causes has been observed in the experiments already carried out, although, of course, it is not possible to detect a small constant error.

The following example illustrates the completeness of the absorption, and the safety of circulating the gas through the apparatus. A value of 79·07 was obtained for the percentage of nitrogen on one occasion. The gas was re-measured next morning under quite different temperature conditions, and the figure deduced was 79·09. The gas was then passed into the phosphorus, well heated, pumped off, and again measured, the percentage found being then 79·08.

Below are given some of the preliminary results obtained for various specimens of air. It will be seen that the agreement for different analyses of the same sample is fairly close. With regard to the absolute value, it would seem that the mean percentage of oxygen is slightly higher than that measured by Regnault (*loc. cit.*), that is, 20·952 at Paris, and 20·949 at Geneva, with a maximum value of 21·00, but it should be very close to the figure 21·00 deduced by Leduc for Paris air.

Results of Some Analyses.

Source of air.	Percentage of oxygen.		
Laboratory, Geneva, 4 p.m., July 11, 1910.........	20·96	20·93	—
,, ,, 5 p.m., ,, 12, ,, ...	20·98	20·95	—
,, ,, (alt. 300 m.) 10 a.m., May 19.	21·02	21·04	21·03
Saleve (alt. 1300 m.) ,, ,, ...	20·95	20·93	—
Rochers de Naye (alt. 2045 m.) ,, ,, ...	21·02	—	—
,, ,, ,, 5·30 a.m.	21·04	—	—

As already mentioned, the few results obtained are merely preliminary, and it is not intended to discuss their bearing on the composition of the atmosphere in the present paper.

In conclusion, I should like to express my best thanks to Professor P. A. Guye, in whose laboratory this work was carried out, for his help in obtaining some of the samples of air analysed, and for the great interest he has taken in the whole work.

TRINITY COLLEGE,
CAMBRIDGE.

CLXVI.—*Tetramethylammonium Hyponitrite and its Decomposition by Heat.*

By PRAFULLA CHANDRA RÂY and HEMENDRA KUMAR SEN.

THE decomposition of tetramethylammonium nitrite by heat has been the subject of a previous communication (Proc., 1911, **27**, 4). It has been shown that although the salt splits up mainly into its constituents, trimethylamine and methyl nitrite, owing to its stability at a fairly high temperature, the substance ultimately becomes charred, resulting in the formation of various secondary products. We thought it therefore desirable to investigate the thermal decomposition of tetramethylammonium hyponitrite, a salt which is the product of a combination of a strong base with a much "weaker" acid.

Preparation:—Pure silver hyponitrite was triturated in a mortar with tetramethylammonium iodide, water being added from time to time. The end-point of the reaction was carefully attained, and the silver iodide filtered off, the filtrate being evaporated in a vacuum over sulphuric acid. It was noticed that the solution, which was practically neutral at first, became more and more alkaline as concentration proceeded, owing to the partial hydrolysis

of the salt. In fact, the presence of free alkali favours the stability of alkali hyponitrites (compare Divers, Trans., 1899, **75**, 113). The crystalline product we obtained was thus a mixture of the hyponitrite with the base tetramethylammonium hydroxide. This circumstance did not interfere with the end we had in view, as tetramethylammonium hydroxide decomposes at a much higher temperature than the hyponitrite; nor could the decomposition products of the hydroxide contaminate those of the hyponitrite in our method of conducting the experiment. The solution of the crystalline mixture gave a yellow precipitate of silver hyponitrite with silver nitrate, and on addition of excess of the latter reagent, a brown precipitate of silver oxide, as might have been expected. That the substance we were dealing with was a tetramethylammonium compound was proved by evaporating a small portion with hydrochloric acid, and converting the hydrochloride into the platinic salt. Two estimations of the percentage of platinum in two distinct preparations gave $Pt = 34{\cdot}83$ and $34{\cdot}95$ respectively, whilst $(NMe_4Cl)_2PtCl_4$ requires $Pt = 35{\cdot}1$ per cent.

Method of Experiment:—The substance was introduced into a bulb provided with an elongated stem. A spiral of glass beads, moistened with the liquid which collects on the surface of glacial phosphoric acid, was interposed between the Sprengel pump and the tube. The use of glacial phosphoric acid has much to recommend it, as we have found it of signal service, not only in arresting the amine base, but also the methyl alcohol formed during the decomposition of the quaternary base, whilst it allows all the indifferent gases to pass through, including methyl ether (compare the earlier paper). The bulb was heated in a bath of sulphuric acid. At 55—60° the salt melts to a clear liquid, but the "click" almost persists. At 75—80° gases begin to be evolved, although very slowly, and the evolution becomes regular at about 110°. This goes on until the temperature is allowed to rise to 140°. At this stage the "click" reappears, and remains persistent up to 190°. It was noticed that a slight residue was left in the bulb, which on examination proved to be a mixture of nitrate and carbonate of the tetramethylammonium base. The carbon dioxide had been absorbed by the hydroxide during exposure, and the nitrate was the result of the decomposition of the hyponitrite. This manner of the decomposition of an alkaline hyponitrite is analogous to that of hyponitrous acid itself, as shown by Rây and Ganguli (Trans., 1907, **91**, 1870). Four distinct preparations were undertaken, and subjected to similar treatment, but the behaviour under the action of heat was much the same. It will be shown below that the substance decomposes according to the following equations:

$$\text{I.}\quad 2NMe_4{\cdot}NO = N_2O + \left[\begin{matrix}NMe_4\\NMe_4\end{matrix}{>}O\right] = N_2O + 2NMe_3 + Me_2O.$$
(Hypothetical.)

$$\text{II.}\ 5NMe_4{\cdot}NO = 2N_2 + NMe_4{\cdot}NO_3 + 2\left[\begin{matrix}NMe_4\\NMe_4\end{matrix}{>}O\right] =$$
(Hypothetical.)

$$2N_2 + NMe_4{\cdot}NO_3 + 4NMe_3 + 2Me_2O.$$

We give here the scheme of a typical analysis of the mixture of gases:

	Volume of gas taken for explosion ...	= 4·7 c.c.
	,, ,, pure oxygen taken ...	=16·4 ,,
Therefore	total volume before explosion	=21·1 ,,
	Volume after explosion	=17·1 ,,
,,	the diminution	= 4·0 ,,
	Volume after absorption by NaOH ...	=12·95 ,,
,,	CO_2	= 4·15 ,,
	Volume after absorption by alkaline pyrogallol	= 2·35 ,,
,,	oxygen unused	=10·6 ,,

The residual 2·35 c.c., or practically 2·4 c.c., of gas were found to be pure nitrogen.

A fresh portion of the gas was next analysed as follows: A drop of concentrated sulphuric acid was introduced into the eudiometer, when the mercury at once began to rise. After the absorption was complete, a reading was taken, which gave the volume of methyl ether, and the volume thus ascertained agreed well with that deduced from explosion. The eudiometer was inverted over water, and shaken vigorously. The water-level began to rise slowly, a characteristic behaviour in the case of nitrous oxide. The residue was found to be pure nitrogen. The proportion of nitrogen to nitrous oxide in almost all the experiments was 1 : 1·5.

The gas, after explosion and absorption of carbon dioxide and oxygen, was found to be pure nitrogen, inasmuch as the nitrous oxide took part in the explosion and yielded up its oxygen, being thereby reduced to its own volume of nitrogen. If the explosive gas be taken to be methyl ether, the following volume relations should exist:

$$\underset{2\text{ vols.}}{Me_2O} + \underset{6\text{ vols.}}{3O_2} = \underset{4\text{ vols.}}{2CO_2} + 3H_2O.$$

That is, eight volumes of mixed gases ought to give four volumes; in other words, there should be a shrinkage of half the volume, which is the same thing as saying that the volume of carbon dioxide produced must be equal to the shrinkage. On comparing the

experiments, this will be found to be actually the case. Since 4·2 c.c. of carbon dioxide were formed, half its volume, namely, 2·1 c.c., must have been methyl ether, and the remaining 2·6 c.c. of the total 4·7 c.c., nitrogen and nitrous oxide. The actual experiment gave 2·4 c.c. of these gases, a difference which is evidently within the limits of experimental error. On comparing the data, it will be found that 10·6 c.c. of oxygen remained unused; hence the amount of used oxygen was $16{\cdot}4 - 10{\cdot}6 = 5{\cdot}8$ c.c. Now, in the combustion of 2·1 c.c. of methyl ether, 6·3 c.c. of external oxygen is necessary, of which 5·8 c.c. were supplied by the pure oxygen, and the rest, 0·5 c.c., by nitrous oxide. This is also a way of indirectly measuring the volume of nitrous oxide present, since nitrous oxide contains half its volume of oxygen. Thus the proportion of nitrogen to nitrous oxide in the particular experiment was as 1·6 : 1. It may be pointed out here that the qualitative and practically the quantitative test for methyl ether with the help of a drop of sulphuric acid or two may well be adopted in gas analysis in the absence of basic gases. The absorption of unsaturated hydrocarbons, for example, ethylene, by concentrated sulphuric acid is at the ordinary temperature very slow, and effective only with fuming sulphuric acid.

The decomposition therefore takes place according to the equations given above. They explain the simultaneous formation of nitrogen and nitrous oxide. Of course, how far one reaction proceeds in preference to the other it is difficult to say, and possibly this varies according to the nature of the experiment. In our experiments, however, we found the reactions proceeding side by side, since the volumes of ether and nitrogen plus nitrous oxide were approximately found to be equal, as required by the above reactions.

Something remains to be said about the concomitant impurity of the hyponitrite, namely, the hydroxide. The decomposition of tetramethylammonium hydroxide has been studied by Hofmann, and later on by Schmidt (*Annalen*, 1892, **267**, 263), and confirmed by ourselves. The products are trimethylamine and methyl alcohol in equivalent proportions:

$$NMe_4{\cdot}OH = NMe_3 + Me{\cdot}OH.$$

The formation of methyl alcohol by the decomposition of the substance we obtained was qualitatively proved by heating a small quantity in a bulb tube with salicylic acid, when the characteristic odour of oil of wintergreen was distinctly perceptible. The methyl alcohol in our experiments was arrested by the phosphoric acid spiral along with the tertiary amine. Blank experiments were made with pure methyl alcohol. A small sealed bulb containing

the alcohol was introduced into a bulb tube connected with the phosphoric acid spiral. After the system was exhausted, the alcohol bulb was broken by a sudden jerk. The alcohol at once rushed into the spiral, but none into the collecting tube.

The amine arrested in the spiral during the experiments was washed out, treated with alkali hydroxide, and subjected to distillation, the distillate being caught in hydrochloric acid. The solution was evaporated to dryness, and the hydrochloride converted into the platinic salt, and analysed. (Found, Pt = 36·85. Calc., Pt = 36·85 per cent.)

It will thus be seen that pure trimethylamine, as demanded by the above equations, was given off.

From the foregoing investigations it is thus established that the products of thermal decomposition of tetramethylammonium hyponitrite are nitrogen monoxide, nitrogen, methyl ether, and trimethylamine; at the same time a small quantity of the hyponitrite is converted into nitrate.

Chemical Laboratory,
Presidency College, Calcutta.

CLXVII.—*Nitrites of the Alkylammonium Bases: Ethylammonium Nitrite, Dimethylammonium Nitrite, and Trimethylammonium Nitrite.*

By Prafulla Chandra Rây and Jitendra Nath Rakshit.

Ethylammonium Nitrite.

The method adopted for the preparation of this salt was exactly the same as that of its lower homologue, namely, double decomposition between mercuric nitrite and ethylamine or interaction between the amine hydrochloride and silver nitrite (compare this vol., p. 1016). The first method gave, however, an altogether unexpected result in that we obtained, not only dimercurammonium nitrite, but, under favourable conditions, diethyltrimercurammonium nitrite, which will form the subject of a separate communication. The filtrate from these mercury compounds was subjected to distillation; the distillate gave copious precipitate of iodoform on treatment with iodine and sodium hydroxide, proving that ethylammonium nitrite was formed, which, during distillation, was decomposed into ethyl alcohol and nitrogen.

As, however, the various primary, secondary, and tertiary amines and their hydrochlorides we had to deal with are not available in this country, we had to undertake their preparation in each instance and test their freedom from impurities, especially ammonia. Our first attempt to prepare pure ethylamine by the reduction of acetonitrile by Mendius' reaction, as improved by Siersch (*Annalen*, 1867, **144**, 139), gave undesirable results. Very considerable quantities of ammonium chloride were simultaneously formed, and the mixture, when extracted with absolute alcohol or a mixture of ether and alcohol, was contaminated with notable proportions of the latter. Ladenburg's modification of the method (reduction by sodium in alcohol) gave a far better yield. In connexion with this we may mention here that the extraction of the amine hydrochloride from a mixture containing sal ammoniac is only successful by Winkler's process (*Annalen*, 1855, **93**, 324) when the former is present in considerable excess. Analysis of the platinichloride showed that the base was pure. (Found, Pt = 39·03. Calc., Pt = 38·93 per cent.)

The filtrate from the interaction of amine hydrochloride and silver nitrite was evaporated in a vacuum as usual. The product obtained, however, was a heavy liquid, which, on immersion in a mixture of salt and ice, could not be solidified. It is remarkable that whilst methylammonium nitrite is a crystalline solid (m. p. 50° approx.), its higher homologue is a liquid. Two distinct preparations were undertaken, the analyses of which are given below:

I. 0·1348 gave 0·1298 CO_2 and 0·1014 H_2O. C = 26·26; H = 8·35.
 0·1770 „ 43·5 c.c. N_2 at 30° and 760 mm. N = 27·70.

II. 0·2450 gave 0·2286 CO_2 and 0·1962 H_2O. C = 25·43; H = 8·89.
 $C_2H_8O_2N_2$ requires C = 26·09; H = 8·69; N = 30·43 per cent.

As the nitrogen was collected in a Schiff's azotometer, the vapour tension was taken to be half the tension of aqueous vapour at that temperature.

The low percentage of nitrogen is accounted for by the fact that during combustion while the air in the tube was being expelled by the current of carbon dioxide, minute bubbles of gas were continuously given off from the liquid nitrite; thus, not only was it a difficult matter to ascertain when the tube was free from air, but traces of the nitrogen were carried away. Estimation of nitrogen by the "Crum Frankland" and "Urea" processes gave the percentage in the two preparations as 15·6 and 15·1 respectively, that is, half the total amount of nitrogen.

Ethylammonium nitrite is a yellow liquid, having a specific

gravity of 1·125 (approx.) at 30° compared with water at the same temperature. Even at the ordinary temperature of the laboratory (23° to 30°) it slowly dissociates. It is soluble in chloroform or alcohol (90 per cent.), and almost insoluble in ether.

Decomposition by Heat:—In the vacuum of the Sprengel pump ethylammonium nitrite slowly decomposes, even at the ordinary temperature; on raising the temperature, the rate of decomposition increases; at 60° it is regular, and at this temperature it is conveniently decomposed. Finally, the temperature was raised to 100° until the "click" became persistent. The small quantity of the liquid which distilled over contained water and ethyl alcohol; the latter being tested by the iodoform reaction. The distillate also responded to the nitroso-reaction. Minute, oily drops, which gave the nitroso-reaction, also condensed in the upper cooler part of the tube. The formation of a nitroso-derivative by the distillation of a primary ammonium nitrite is, no doubt, striking. Linnemann also noticed the simultaneous formation of *iso*propyl alcohol and nitrosodipropylamine by heating the aqueous solution of propylammonium nitrite (*Annalen*, 1872, **161**, 47). Accepting Linnemann's view, we provisionally explain the formation of nitrosoalkylamine according to the equation:

$$2R\cdot NH_3\cdot NO_2 = N_2 + 3H_2O + R_2N\cdot NO,$$

where *R* represents an alkyl radicle. It may be mentioned here that in the case of methylammonium nitrite also a corresponding nitrosoamine is obtained. The gaseous mixture consisted of nitrogen and nitric oxide, with traces of free ethylamine.

Dimethylammonium Nitrite.

This compound, prepared as before by the interaction of silver nitrite and the corresponding amine hydrochloride* and evaporation in a vacuum of the filtrate, was a pale yellow, transparent liquid:

0·3389 gave 0·3716 CO_2 and 0·2763 H_2O. C = 25·39; H = 9·08.
0·1685 ,, 42·0 c.c. N_2 at 29° and 760 mm. N = 28·30.
$C_2H_8O_2N_2$ requires C = 26·09; H = 8·69; N = 30·43 per cent.

The result for nitrogen is rather low, as in the case of the previous salt, for reasons assigned thereunder. When estimated by the "Crum Frankland" and "Urea" processes, the percentage was 14·75, that is, nearly half the total amount.

Decomposition by Heat:—The salt decomposes slightly at the

* The platinum salt of two distinct preparations gave Pt = 39·15 and 39·05. Calc., Pt = 38·93 per cent.

ordinary temperature in a vacuum; at 60° the decomposition is fairly regular; the gaseous products are nitrogen and a trace of free dimethylamine. In the distillate, methyl alcohol was also detected. Evidently the nitrogen and methyl alcohol were formed according to the following equation:

$$NH_2Me_2{\cdot}NO_2 = 2MeOH + N_2.$$

In some cases a small quantity of nitric oxide was detected. The main portion of the salt was, however, converted into nitrosodimethylamine, which gave Liebermann's nitroso-reaction, and its boiling point was found to be 144° (approx.) * by Jones' method (Trans., 1878, **33**, 175). There was a slight solid residue, which was not decomposed at 100°, and this proved to be a nitrate. Dimethylammonium nitrite is stable at 21° to 23°. When first prepared, in January last, the laboratory temperature was 21°. After an interval of two months, during which period the temperature of the laboratory gradually increased to 30°, a portion of the substance was converted into the nitroso-compound. An estimation of "nitritic" nitrogen by the "Urea" process showed that 76·73 per cent. was real nitrite. It may be pointed out here that the nitroso-compound does not respond to the "Urea" test.

Trimethylammonium Nitrite.

The trimethylamine which was required for the purpose was prepared by the dry distillation of tetramethylammonium hydroxide in a current of dry hydrogen (Schmidt, *Annalen*, 1892, **267**, 263). Analysis of the platinichloride showed that the base was pure. (Found, Pt = 36·72. Calc., Pt = 36·85 per cent.)

The method of preparation of the nitrite was exactly the same as in the preceding cases. The salt was obtained in beautiful pale green crystals. It was extremely deliquescent:

0·1275 gave 0·1496 CO_2 and 0·1077 H_2O. C = 32·00; H = 9·38.
0·0818 ,, 9·8 c.c. N_2 ("nitritic") (moist) at 23° and 760 mm.
N ("nitritic") = 13·44.

$C_3H_{10}O_2N_2$ requires C = 33·98; H = 9·39; N = 13·20 per cent.

Decomposition by Heat:—The salt slowly and continuously dissociates into trimethylamine and nitrous acid, even at the ordinary temperature. The nitrous acid in turn breaks up according to the equation:

$$3HNO_2 = HNO_3 + H_2O + 2NO.$$

The nitric acid thus generated combines with a portion of the

* The substance contained a trace of moisture which had the effect of lowering the boiling point.

free amine (the product of dissociation), resulting in the formation of trimethylammonium nitrate. It is for this reason that a perfect vacuum cannot be obtained when a tube containing the salt is attached to the Sprengel pump. Minute bubbles are given off, which interfere with the persistency of the "click." When the temperature is slowly raised, the rate of decomposition increases. At 55° the salt melts to a pale green, viscous liquid, from which bubbles continually escape. As water is one of the products of decomposition, the melting point of the salt cannot be accurately determined. On withdrawing the bath, the molten substance solidifies *en masse* to its original crystalline structure and green colour. The decomposition is effected conveniently at 100°. During this stage minute drops of a colourless liquid condensed in the upper part of the tube, which, after the completion of the decomposition and removal of the bath, solidified to a thin, white layer. An appreciable quantity of residue was left in the tube.

The gaseous mixture which was collected consisted of equal volumes of trimethylamine and nitric oxide, with traces of nitrogen. That it was trimethylamine was proved by its absorption by hydrochloric acid and the conversion of the hydrochloride into the platinic salt. (Found, Pt = 37·37. Calc., Pt = 36·85 per cent.)

The white, crystalline residue which was not decomposed at 100° was shown by analysis to consist of slightly impure trimethylammonium nitrate. (Found, C = 26·20; H = 8·07; N = 21·90. Calc., C = 29·50; H = 8·19; N = 23·10 per cent.)

The decomposition evidently proceeds according to the equation:

$$3NHMe_3{\cdot}NO_2 = NHMe_3{\cdot}NO_3 + 2NO + 2NMe_3 + H_2O.$$

A sample of trimethylammonium nitrite prepared in December last (the temperature of the laboratory being 21°) was found on examination in the middle of March (temp. 30°) to consist of 51 per cent. of nitrite and 49 per cent. of nitrate.

Concluding Remarks on the Alkylammonium Nitrites:—It will be evident from the present investigation that, not only the primary, but the secondary and tertiary amines also yield the corresponding nitrites. The order of stability of these salts is what might have been expected from the heat of neutralisation of these organic bases with hydrochloric acid. Thus, methylamine and ethylamine evolve 26,000 calories in round numbers, whilst dimethylamine and trimethylamine evolve 23,000 and 17,000 calories respectively. The primary ammonium nitrites have been found to be the most stable, and trimethylammonium nitrite the least; the latter, in fact, undergoes complete dissociation into nitrous acid and trimethylamine. All ammonium nitrites, however, dis-

sociate more or less, even at the ordinary temperature, and if these nitrites are kept in a desiccator in an open dish they slowly find their way into the sulphuric acid, being ultimately completely absorbed by this reagent. In a vacuum desiccator this absorption takes place more rapidly.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

CLXVIII.—*Nitrites of the Benzylammonium Series. Benzylammonium Nitrite and Dibenzylammonium Nitrite and their Sublimation and Decomposition by Heat.*

By PRAFULLA CHANDRA RÂY and RASIK LAL DATTA.

Benzylammonium Nitrite.

IN continuation of the work on the aliphatic amine nitrites, we were led to the study of the nitrites of the benzylammonium series, and it appears that the nitrites of this series are more stable than the corresponding nitrites of the aliphatic amines. The first of the series, namely, monobenzylammonium nitrite, was prepared as usual by the double decomposition of silver nitrite and monobenzylamine hydrochloride and evaporation of the resulting solution in a vacuum over sulphuric acid. Monobenzylamine hydrochloride was prepared according to Mason's method (Trans., 1893, **63**, 1311) by the action of alcoholic ammonia on benzyl chloride, which gave very satisfactory results.

The salt as prepared in the above manner is of a pale yellow colour, and consists of crystalline plates. It is hygroscopic and stable. It is soluble in alcohol, ether, or benzene. Unlike the alkylammonium nitrites, it does not decompose into its constituents, and even undergoes sublimation in a vacuum. It is very remarkable that an amine nitrite with a very heavy group, $C_6H_5\cdot CH_2\cdot$, is more stable than amine nitrites with such lighter groups as methyl, ethyl, etc.; on the other hand, ammonium nitrite in which no atom of hydrogen is substituted is more stable than the alkyl-substituted ammonium nitrites, so much so that the former can be sublimed, whilst the latter have no tendency to sublime, and are easily decomposable. In the case of benzyl-

ammonium nitrite it is the substitution of the phenyl in the methyl group that determines its stability and subliming property. As a rule, aromatic compounds are especially endowed with such a property.

Analysis of benzylammonium nitrite gave the following results:

0·3614 gave 0·7002 CO_2 and 0·2164 H_2O. C=52·85; H=6·65.

0·1216 „ 19·7 c.c. N_2 (moist) at 30° and 760 mm. N=17·94.

$C_7H_{10}O_2N_2$ requires C=54·54; H=6·49; N=18·18 per cent.

The "nitritic" nitrogen, as estimated by the "Crum Frankland" and "Urea" methods, gave 8·86 per cent. instead of 9·09, that is, half the total nitrogen required by theory.

Sublimation and Decomposition by Heat:—When the salt was heated in a Sprengel vacuum (compare Rây, Trans., 1909, **95**, 345) it began to sublime at 80°, and on maintaining the temperature of the bath between 80° and 85°, practically the whole of the substance sublimed, and was deposited on the upper and cooler parts of the tube in beautiful white, stellate clusters of crystals. It is noteworthy that whilst the salt as originally prepared has a pale yellow tint, the sublimed crystals are colourless. An estimation of "nitritic" nitrogen of the sublimate gave 9·07 per cent. instead of 9·09 as required by theory. In this connexion, an interesting fact was discovered. The tube containing the sublimate was kept in a vacuum in an open bottle over sulphuric acid; on the next day, the bottle containing the tube was found to be lined with white clouds of the salt. This proves that the substance (once sublimed) very slowly sublimes in a vacuum at the ordinary temperature (30°).

If, instead of keeping the temperature between 80° and 85°, the bath is heated to a higher temperature, the salt melts, and begins to decompose into benzyl alcohol and nitrogen according to the equation:

$$C_6H_5{\cdot}CH_2{\cdot}NH_3{\cdot}NO_2 = C_6H_5{\cdot}CH_2{\cdot}OH + H_2O + N_2,$$

a decomposition which takes place at once when the hydrochloride is directly treated with nascent nitrous acid (sodium nitrite and sulphuric acid).

The benzyl alcohol was recognised by its odour and by conversion into benzaldehyde and benzoic acid by nitric acid and alkaline permanganate respectively. The nitrogen was found to be free from nitric oxide. A quantitative experiment gave N=14·45, instead of 19·18 per cent., as required by theory. The deficit was due to a small part of the substance subliming unchanged, and being carried off as fine dust into the "fall-tube" and thus escaping decomposition.

Dibenzylammonium Nitrite.

The dibenzylamine hydrochloride was prepared simultaneously with monobenzylamine hydrochloride, according to Mason's method, since both are formed at the same time by the action of alcoholic ammonia on benzyl chloride. Double decomposition between the amine hydrochloride in aqueous solution and silver nitrite gave the corresponding amine nitrite. The solution was evaporated in a vacuum over sulphuric acid, and the salt was obtained in white scales. It was not deliquescent, and was somewhat sparingly soluble in water, but readily soluble in ether or alcohol:

0·1629 gave 0·4020 CO_2 and 0·0958 H_2O. C = 67·30; H = 6·54.
Found: N (nitritic) = 6·15.

$C_{14}H_{16}O_2N_2$ requires C = 68·85; H = 6·56; N = 5·74 per cent.

Sublimation and Decomposition by Heat:—The substance was heated in the Sprengel vacuum, and it simultaneously melted and sublimed at about 110°. On maintaining the temperature at this point for some time, the molten mass disappeared, a white, crystalline sublimate was deposited in the cooler parts of the tube, and a small quantity of gas was collected, which was found to be almost pure nitric oxide. A thin but distinct layer of a crystalline solid was left behind. It was found on examination to be dibenzylamine nitrate. Viscid, oily drops were also deposited just below the sublimate. This liquid turned red litmus blue. Evidently it was dibenzylamine, which boils at 300° under the ordinary pressure, but at about 180° in a vacuum. The sublimate was found to be dibenzylamine nitrite. Traces also were carried off into the "fall tube," which was washed with alcohol, and the solution responded to the test for a nitrite. The major portion of the salt thus sublimed unchanged; a small fraction undergoes decomposition according to the equation:

$$3(C_6H_5{\cdot}CH_2)_2NH_2{\cdot}NO_2 = (C_6H_5{\cdot}CH_2)_2{\cdot}NH_2{\cdot}NO_3 + 2NO + H_2O + 2(C_6H_5{\cdot}CH_2)_2NH.$$

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

CLXIX.—*The Density of Liquid Sucrose and of its Solutions in Water.*

By Frederik Schwers.

The densities of aqueous solutions of sucrose have been carefully determined by Gerlach (*Dingl. polyt. J.*, 1864, **172**, 35) for seven different concentrations and between 0° and 100°. With the object of continuing my previous researches on binary mixtures (*Bull. Acad. roy. Belg.*, 1908, 814; *Rec. trav. chim.*, 1909, **28**, 261; *J. Chim. phys.*, 1911, **9**, 15), and calculating the variations undergone by the volume-contractions with the temperature, it was first of all necessary to obtain data on the density of sucrose in the liquid and superfused state. On its passage into solution, sucrose, like any other solid, occupies the volume it would have in the liquid state at the temperature of the dissolution; Wulff (*Zeitsch. f. die ges. Rübenzuckerindustrie*, 1887, **37**, 918) has already called attention to this point. I could not find, however, any such determinations in the extensive literature relating to this subject; in view of the great number of chemists who have studied sucrose, this can only be explained by the great experimental difficulties of determinations of this kind.

Several investigators have tried to obtain an approximate value by means of extrapolation from the density curve of aqueous sucrose solutions. This value is between 1·5549 and 1·56165 *; but we cannot place much reliance in these numbers, owing to the fact, to which Plato (*Zeitsch. f. die ges. Rübenzuckerindustrie*, 1900, **50**, 1098) has already called attention, that it is impossible to prepare solutions stronger than 76 per cent., and that an extrapolation, which extends over nearly 25 per cent., can only give a rough approximation. It may be added that it is impossible to find out in this way the expansion-coefficient of liquid sucrose.

The greatest experimental difficulties were to melt the sucrose without the slightest decomposition, and to maintain it in the superfused state for sufficient time to make all the determinations.

According to Braconnet (*Ann. Chim. Phys.*, 1821, [ii], **16**, 427), sucrose melts to a clear liquid when carefully heated in the neighbourhood of its melting point, but in spite of careful purification of the sucrose by fractional precipitation of the aqueous solution with ethyl alcohol, and very slow heating in an oil-bath, I could

* See the complete data on this subject in *Die Chemie der Zuckerarten* by E. von Lippmann, 1904, 3rd ed. Braunschweig.

not avoid a slight decomposition whenever the sucrose was exposed to air.

After a long series of unsuccessful attempts, I at last secured the desired result by melting finely pulverised sucrose under a liquid. This mode of procedure avoids charring due to superheating, diminishes oxidation by contact with air, and, moreover, favours retention in the liquid state. The liquid used must be without chemical or physical action on sucrose; it must be non-oxidising, and possess a boiling point above the melting point of saccharose. Of all the liquids tried, I found liquid paraffin the most convenient (b. p. about 190°).

The pyknometer used was a small flask of Jena-glass of about 50 c.c. capacity, the neck of which had been drawn out and marked. The powdered sugar was first introduced and weighed, the flask filled with paraffin, and carefully heated until the melting point was reached. The apparatus was then placed in a thermostat, which was kept very constant, and the paraffin adjusted to the mark. The weight was taken when the apparatus had reached the temperature of the balance room. The density of the paraffin used was previously determined in the same apparatus, the volume of which was ascertained by filling with water. All the experiments were made at the same temperature in order to eliminate errors due to the imperfections of the method. Needless to say, all the weighings were reduced to a vacuum—an important correction in the case of such large quantities.

By this method I was able to determine the density of sucrose down to $-15°$, without crystallisation; the sugar becomes more and more viscous, and ultimately hard like glass, which we may also regard as being in the superfused state.

The densities, compared with water at 4°, are as follows:

$t°$.	$d\ t°/4°$.	$t°$.	$d\ t°/4°$.
−14·55	1·51966	45·85	1·50605
0·00	1·51915	59·00	1·49812
14·00	1·51756	77·85	1·48493
20·55	1·51663	101·55	1·46790
33·75	1·51245	114·70	1·45846

Or, taking the volume at 0° as unity, the volumes at the other temperatures are as follows:

$t°$.	Vol. $t°/0°$.	Variation per degree.	$t°$.	Vol. $t°/0°$.	Variation per degree.
−14·55	0·99966	0·000023	45·85	1·00870	0·000406
0·00	1·00000	0·000075	59·00	1·01404	0·000478
14·00	1·00105	0·000093	77·85	1·02305	0·000500
20·55	1·00166	0·000210	101·55	1·03490	0·000510
33·75	1·00443	0·000353	114·70	1·04161	

Between 35° and 115° the dilatation is almost regular (see

diagram II), and approximately four times that of solid sucrose according to Joule and Playfair (*Quart. Journ. Chem. Soc.*, 1848, **1**, 121), who give 0·0001116 between 0° and 100°. Below this temperature, however, it diminishes rapidly, although regularly; between 15° and 20° it attains the value of that of solid sucrose, and between 0° and −15° it is very much less.

The rapid bending of the curve led me first to suppose the existence of a real density-maximum, as in the case of water: but after a large number of very careful experiments, I came to the conclusion that the curve is as shown in the figure; so that, if there is really a density-maximum, it has not been reached at the temperature of −15°. Unfortunately, the method used does not permit investigations at lower temperatures with the same degree of exactness. The reservoir above the mark ought to be much larger to allow the expansion of the paraffin, owing to the fact that the weighing must be done at the ordinary temperature, and it would be difficult to avoid slight loss by evaporation; moreover, there is a practical obstacle, due to the solidification of the paraffin.

The calculation of an analytical form of the curve V_t would involve much work, owing to its sinuosity, without giving any explanation of the particular form of the curve; the nature of the phenomena is sufficiently well indicated by the graphic representation.

The experiments were not continued beyond 115°, because it is more difficult to obtain the same degree of accuracy, and also because the maintenance during several hours at a temperature so near to the melting point initiates charring and decomposition. It appears quite certain that the continuation of the curve approximates to a straight line.

It is between 35° and 40° that the great change in the dilatation occurs. It may be interesting to point out that superfused sugar possesses down to 38° a certain fluidity, so that it is still possible to draw it out in threads, whereby crystallisation takes place, as was first observed by Dumas. Below this temperature, the viscosity becomes so great that the substance has the appearance of a solid.

For liquids with non-associated molecules only, the variations of the volume with the temperature may be represented on a diagram by a straight line. With liquids forming physical aggregates (which is the general case), the volume-curve becomes more nearly parallel to the abscissa with decreasing temperature at a point which is peculiar to the liquid in question.

In a previous paper (*J. Chim. phys.*, 1911, **9**, 72) I have shown that the hypothesis of De Heen, elaborated afterwards by Van Laar, gives the best explanation of the facts. We have to consider

the volume-changes of a liquid by heating as the result of two opposite actions: the heat gives more energy to the molecules, and increases the volume, but, on the other hand, the partial depolymerisation—or physical dissociation—of the aggregates produces a decrease of volume.

Water has been, so far, the only liquid known for which the second of these actions exceeds the first (between 0° and 4°); as is now seen, liquid sucrose approaches very nearly to water in this respect, and is perhaps quite similar at lower temperatures. As I have already pointed out in the above-mentioned paper, the presence of a real density-maximum is not a sufficient reason for placing a liquid in a special class; this maximum shown by water is only an external manifestation—in a higher degree—of a property which is common to all associated liquids.

It appears from observations on a large number of liquids that the presence of hydroxyl groups in the molecule is particularly favourable to physical association; no wonder that sugar (with its large number of these groups) possesses more associating power than the alcohols.

If similarity in the form of the V_t-curve permits us to assume a similar state of polymerisation, it would appear from this study that water possesses a much higher degree of association than we have hitherto believed—higher than that of sucrose, of which the smallest molecule has ten hydroxyl groups.

Aqueous Solutions of Sucrose.

As already mentioned, it was of interest to determine the departure shown by the different water-sucrose mixtures from the theoretical density, as calculated from the well-known formula:

$$d_v = \frac{p_1 + p_2}{\dfrac{p_1}{d_1} + \dfrac{p_2}{d_2}} \quad \text{or} \quad d_v = \frac{p_1 + p_2}{v_1 + v_2}.$$

If we calculate from the density of *solid* sucrose (which is approximately 1·59), we find a slight contraction up to 63 per cent. of sucrose, and a dilatation for solutions of higher concentration. Plato (*Zeitsch. f. die ges. Rübenzuckerindustrie*, 1900, **50**, 1098), however, admitted that the volume contraction must be calculated from the value of *liquid* sucrose. Using the number he obtained by extrapolation from aqueous solutions (1·55626 at 17·5°), he concluded that all the solutions exhibit contraction, which is a maximum (1·37 per cent.) at a concentration of nearly 60 per cent. of sucrose. It might be first objected that, for our purpose, the method is not sufficiently accurate to determine the dilatation-

coefficient of liquid sucrose, which is quite necessary to calculate the volume-contraction of the solutions up to 100°. As, on the other hand, it has just been shown that experiment gives a density quite different (less than 1·52) from the extrapolated value (1·55 to 1·56), it is clear that experimental verification was necessary. It follows that the volume-contraction is much more pronounced than would appear from Plato's calculations. In the following tables are given the calculations I have made from Gerlach's experimental data (*loc. cit.*). The numbers for density d reproduced in the first column are from experimental observation, and not the interpolated values; I have given these, as Gerlach did, to six places of decimals, although I think that the last place might, for our purpose, be omitted. The densities are referred to water at $17·5° = 1$; it was needless to transform those in the values $d\ t°/4°$, because the final result C_v is the same in both cases. As in the tables already published, d is the observed, and d_v the theoretical density; the volume contraction is readily calculated from the formula $1 - d_v/d$.

Sucrose: 10 *per cent.* + *Water:* 90 *per cent.*

$t°$.	$d\ t°/17·5°$.	d_v.	d_v/d.	C_v.
0·9	1·041792	1·036112	0·99455	0·545
9·2	1·041356	1·036176	0·99502	0·498
12·4	1·040948	1·035955	0·99520	0·480
15·3	1·040521	1·035571	9·99524	0·476
17·5	1·040104	1·035366	0·99544	0·456
25·5	1·038037	1·033772	0·99589	0·411
32·4	1·035961	1·031895	0·99607	0·393
43·3	1·031848	1·028091	0·99636	0·364
52·6	1·027764	1·024150	0·99658	0·342
60·9	1·023710	1·020136	0·99651	0·349
68·7	1·019686	1·015822	0·99621	0·379
75·9	1·015691	1·011682	0·99605	0·395
82·4	1·011725	1·007666	0·99599	0·401
88·5	1·007788	1·003833	0·99607	0·393
94·3	1·003880	1·000224	0·99637	0·363
99·9	1·000000	0·996650	0·99665	0·335

Sucrose: 20 *per cent.* + *Water:* 80 *per cent.*

5·9	1·085477	1·074283	0·98969	0·031
17 5	1·083234	1·073324	0·99085	0·915
31·6	1·078779	1·070028	0·99188	0·812
42·6	1·074356	1·065889	0·99212	0·788
52 0	1·069965	1·062065	0·99262	0·738
60·8	1·065605	1·057635	0·99252	0·748
68·9	1·061278	1·053153	0·99234	0·766
76·3	1·056982	1·048619	0·99209	0·791
89·3	1·048482	1·040460	0·99235	0·765
95·6	1·044278	1 036499	0·99255	0·745

Sucrose: 30 *per cent.* + *Water:* 70 *per cent.*

$t°$.	$d\ t°/17·5°$.	d_v.	d_v/d.	C_v.
9·2	1·131996	1·115026	0·98501	1·499
17·5	1·129586	1·114169	0·98635	1·365
31·2	1·124800	1·110986	0·98772	1·228
42·4	1·120048	1·106745	0·98812	1·188
52·0	1·115330	1·102421	0·98842	1·158
61·0	1·110646	1·097835	0·98847	1·153
69·3	1·105995	1·092933	0·98819	1·181
77·2	1·101377	1·088311	0·98813	1·187
84·5	1·096792	1·083684	0·98805	1·195
91·3	1·092240	1·079389	0·98823	1·177
97·9	1·087721	1·075070	0·98837	1·163

Sucrose: 40 *per cent.* + *Water:* 60 *per cent.*

−0·18	1·184531	1·159245	0·97865	2·135
9·8	1·181945	1·159102	0·98067	1·933
17·5	1·179358	1·158252	0·98210	1·790
30·9	1·174222	1·155094	0·98371	1·629
42·0	1·169121	1·150642	0·98420	1·580
52·0	1·164056	1·146050	0·98453	1·547
61·0	1·159026	1·141318	0·98472	1·528
69·6	1·154032	1·136145	0·98450	1·550
78·0	1·149073	1·131149	0·98440	1·560
85·9	1·144150	1·126074	0·98420	1·580
93·3	1·139261	1·121392	0·98432	1·568

Sucrose: 50 *per cent.* + *Water:* 50 *per cent.*

1·96	1·238293	1·207088	0·97489	2·511
17·5	1·232748	1·206054	0.97834	2·166
30·4	1·227241	1·202935	0·98019	1·981
41·9	1·221771	1·198184	0·98069	1·931
52·2	1·216339	1·193172	0·98095	1·905
61·8	1·210945	1·187974	0·98103	1·897
70·9	1·205589	1·182117	0·98053	1·947
79·5	1·200269	1·177134	0·98072	1·928
87·6	1·194986	1·171829	0·98062	1·938
95·3	1·189740	1·166975	0·98087	1·913

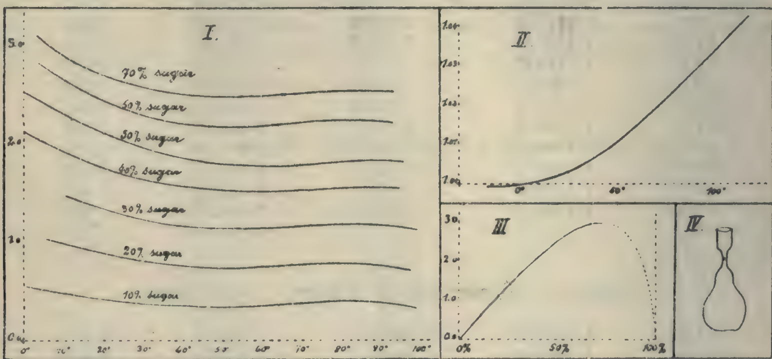
Sucrose: 60 *per cent.* + *Water:* 40 *per cent.*

3·1	1·295890	1·259105	0·97161	2·839
17·5	1·289952	1·257773	0·97505	2·495
30·7	1·284054	1·254806	0·97722	2·278
42·4	1·278197	1·249386	0·97741	2·259
52·9	1·272379	1·244075	0·97768	2·232
62·9	1·266600	1·238467	0·97779	2·221
72·5	1·260861	1·232593	0·97758	2·242
81·5	1·255161	1·226804	0·97741	2·259
90·1	1·249500	1·221396	0·97751	2·249
98·4	1·243877	1·215669	0·97732	2·268

Sucrose: 70 *per cent.* + *Water*: 30 *per cent.*

$t°$.	$d\ t°/17·5°$.	d_v.	d_v/d.	C_v.
3·3	1·357518	1·315594	0·96912	3·038
17·5	1·351168	1·314240	0·97267	2·733
31·0	1·344860	1·310629	0·97455	2·545
43·8	1·338594	1·304781	0·97474	2·526
55·1	1·332370	1·298765	0·97478	2·522
65·5	1·326188	1·292790	0·97482	2·518
75·0	1·320046	1·286652	0·97470	2·530
84·4	1·313946	1·280357	0·97444	2·556
93·4	1·307887	1·274543	0·97450	2·550

The diagram on which these values are plotted shows—better than the numbers—the variations of C_v for each mixture of sucrose and water. The general form of the curves (they are very similar



I. *Abscissae*: *Temperature.*
Ordinates: *Contraction in percentage of the initial volume.*

II. *Abscissae*: *Temperature.*
Ordinates: *Volume of liquid sucrose* (*volume at* 0° = 1).

III. *Abscissae*: *Weight per cent. of sugar.*
Ordinates: *Volume contraction* (*at* 0°) *in percentage of the initial volume.*

IV. *Pyknometer used for the density determinations.*

for all the concentrations) shows a diminution of the contraction up to nearly 50°; then each curve becomes parallel to the abscissa, and an increase of contraction takes place with a maximum at about 80°. After the bend, the curve descends again at higher temperatures.

This behaviour is analogous to that previously observed in other binary mixtures, and especially described in my papers on the aqueous solutions of the different alcohols. By comparing the forms of the contraction curves of mixtures of water with ethyl alcohol, glycol, and glycerol, I observed that the bends become more marked

as the number of hydroxyl groups increases; on the other hand, that the maximum occurs at higher temperatures as the boiling points of the alcohol rise.

In the case of sucrose, the incurvation is rather pronounced, but not in proportion to the large number of hydroxyl groups; the form of the curves is not very different from that of the system glycerol + water, and the maximum occurs at nearly the same temperature (about 80°).

Similar remarks apply to other properties. For example:

(1) If we consider, for the pure liquids, the portion of the V_t-curve which is nearly a straight line, we see that the volume change for 1° is approximately as follows (the volume at 0° being = 1):

Ethyl alcohol	0·0013
Glycol	0·00085
Glycerol	0·0006

For sucrose, the value 0·0005 (approx.) was found, which approaches very closely to the number for glycerol. It may here be recalled, as a general rule, that the largest differences in physical properties occur in organic compounds with fewest carbon-atoms, and that these differences diminish as the carbon-chain lengthens.

(2) If we consider, at the same temperature, the volume contraction of the mixtures with water, we see that it is very large for the monatomic alcohols, but decreases with increase in the number of hydroxy-groups. The contraction-maximum at 0° is, for instance:

For ethyl alcohol + water	4·00 per cent.
,, glycol ,, ,,	1·55 ,,
,, glycerol ,, ,,	1·38 ,,

With sucrose solutions an important contraction (more than 3 per cent.) occurs at a concentration of 70 per cent.; according to the curve (No. III), a more concentrated solution would give a higher contraction. But experiment fails, because water and sucrose are not miscible in all proportions at the ordinary temperature.

As a general rule, the contraction-maximum occurs at a higher concentration as the molecular weight of the substance increases; so that it is quite natural that this maximum is not yet reached at the concentration of 70 per cent. of sugar. By transforming the weight-percentage into molecular-percentage, this maximum would, of course, be displaced to the left; but by doing so, we would seem to accept as true, a priori, the theory that admits the existence of combinations in molecular proportions for determined concentrations; I have (*J. Chim. phys.*, 1911, **9**, 57) discussed the reasons against thinking that there is up to the present any evidence of the existence of such combinations.

The change of association that occurs on mixing two liquids is

generally a maximum when the liquids are in nearly the same proportions or in simple molecular relations; it is natural that the volume-change—whatever the reasons of this change may be—should be more pronounced in concentrated than in dilute solutions: but that is not a sufficient reason for assuming the existence of chemical combinations in the solution.

These investigations should be completed by the examination of other substances of the sugar class, and of their solutions in water; the highly associated properties of these compounds promise interesting results.

I desire to express my best thanks to the Committee of Managers for permission to work in the Research Laboratory of the Royal Institution of Great Britain.

DAVY-FARADAY RESEARCH LABORATORY,
LONDON.

CLXX.—*Triketohydrindene Hydrate. Part V. The Analogues of Uramil and Purpuric Acid.*

By SIEGFRIED RUHEMANN.

2-OXIMINO-1:3-DIKETOHYDRINDENE, $C_6H_4<^{CO}_{CO}>C:NOH$, which may be regarded as the violuric acid of the hydrindene group, on treatment with fuming hydriodic acid, yields hydrindantin instead of diketohydrindamine (this vol., p. 1306). The transformation of the oxime into the amine takes place, however, when stannous chloride is used as reducing agent. The base, $C_6H_4<^{CO}_{CO}>CH\cdot NH_2$, which is the analogue of uramil, is very unstable, turning brown and then blue on exposure to moist air. Owing to this property, it was not possible to obtain it in a pure state and to verify its composition by analysis, but it could be characterised by the condensation products which it forms with aromatic aldehydes and triketohydrindene hydrate. With benzaldehyde, it condenses to 1:3-*diketo-2-benzylidenehydrindamine*, $C_6H_4<^{CO}_{CO}>CH\cdot N:CH\cdot C_6H_5$, which is orange; with salicylaldehyde, anisaldehyde, and *p*-dimethylaminobenzaldehyde, it yields substances which are of a deeper colour. These compounds, although stable when dry, are hydrolysed gradually by moist air, but readily on boiling with water or alcohol,

with the production of aldehyde and amine, dark solutions being formed, which, under the influence of the oxygen of the air, turn blue. This behaviour of diketohydrindamine resembles 4-amino-1-phenyl-3-methylpyrazolone, $C_6H_5\cdot N{<}\begin{matrix}N{=}C\cdot CH_3\\ CO\cdot CH\cdot NH_2\end{matrix}$, the uramil of the pyrazolone series. Knorr (*Annalen*, 1887, **238**, 189), who obtained this base by reduction of the corresponding oxime, did not succeed in isolating it; he proved, however, its formation by the analysis of its hydrochloride, and the study of its condensation products with benzaldehyde and 4-keto-1-phenyl-3-methylpyrazolone, $C_5H_5\cdot N{<}\begin{matrix}N{=}C\cdot CH_3\\ CO\cdot CO\end{matrix}$. He also indicated the resemblance between the compound which is formed by the action of the diketopyrazole on the amine, and purpuric acid by showing that it yields deep violet solutions with alkalis or ammonia. The constitution of this substance, which was called rubazonic acid, may be represented thus:

$$\begin{matrix}N{=}CMe\\ NPh\cdot CO\end{matrix}{>}CH\cdot N{:}C{<}\begin{matrix}CMe{:}N\\ CO{-}NPh\end{matrix}.$$

This formula corresponds with that of purpuric acid put forward seven years later by Piloty (*Annalen*, 1904, **333**, 68) and by Slimmer and Stieglitz (*Amer. Chem. J.*, 1904, **31**, 661). The condensation product formed by diketohydrindamine with triketohydrindene hydrate, which may be called *diketohydrindylidene-diketohydrindamine*, resembles purpuric and rubazonic acids both in constitution:

$$C_6H_4{<}\begin{matrix}CO\\ CO\end{matrix}{>}CH\cdot N{:}C{<}\begin{matrix}CO\\ CO\end{matrix}{>}C_6H_4,$$

and in properties; it differs from those acids mainly in the degree of stability. Although it can be isolated from its ammonium salt on careful treatment with dilute hydrochloric acid, it is very sensitive towards mineral acids and alkalis; purpuric acid, however, does not exist in the free state, whereas rubazonic acid is comparatively stable, being decomposed only on boiling its alkaline solutions. The ammonium salt of the hydrindene analogue of purpuric acid may be represented by the formula:

$$C_6H_4{<}\begin{matrix}CO{-}{-}{-}{-}\\ C(ONH_4)\end{matrix}{\geqslant}C\cdot N{:}C{<}\begin{matrix}CO\\ CO\end{matrix}{>}C_6H_4.$$

which corresponds with Slimmer and Stieglitz's formula of murexide. It is formed by the oxidation of diketohydrindamine, and can readily be obtained from hydrindantin under conditions similar to those which Piloty and Finckh (*Annalen*, 1904, **333**, 27) recommend for the preparation of murexide from alloxantin. The

salt is characterised by its property of dissolving in water to yield deep blue solutions. The mode of formation of purpuric acid and its analogues leads to the view that similar substances would be produced by the action of the cyclic di- or tri-ketone with uramil or its analogues. Such a substance can readily be prepared in the form of its potassium salt on treatment of a solution of uramil in potassium hydroxide with triketohydrindene hydrate. This salt of *diketohydrindylideneuramil*, $CO<\begin{matrix}NH\text{——}CO\\NH\cdot C(OK)\end{matrix}\gg C\cdot N:C<\begin{matrix}CO\\CO\end{matrix}>C_6H_4$, dissolves in water to form reddish-violet solutions, which are decolorised immediately on the addition of dilute hydrochloric acid.

The ease with which hydrindantin is transformed into the analogue of murexide, together with Strecker's results concerning the formation of murexide by the action of amino-acids on alloxan (*Annalen*, 1862, **123**, 363), suggested that the blue colour reaction which triketohydrindene hydrate gives with proteins and their hydrolytic products, is due to the production of the ammonium salt of diketohydrindylidenediketohydrindamine. This view, which is supported by the fact that in both cases the coloration is accompanied by the formation of aldehydes, has been confirmed by the isolation of the salt from the product of the action between alanine and triketohydrindene hydrate. After this substance had been recommended as a reagent for amino-acids (Trans., 1910, **97**, 2025; see also Abderhalden and Schmidt, *Zeitsch. physiol. Chem.*, 1911, **72**, 37), Hurtley and Wootton (this vol., p. 288) expressed the opinion that alloxan will be found of great use in biochemistry, and they based their view on Strecker's results. It appears, however, that alloxan is less valuable for the purpose than triketohydrindene hydrate on account of the inferior sensitiveness of the colour test, especially in the examination of animal fluids (for example, urine), and for the reason that it also gives with ammonia the murexide reaction, which is probably due to the presence of traces of alloxantin in alloxan.

Experimental.

1 : 3-*Diketohydrindamine*, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CH\cdot NH_2$.

On gradually adding finely powdered oximino-1 : 3-diketohydrindene (5 grams) to stannous chloride (15 grams), dissolved in concentrated hydrochloric acid (30 c.c.), it slowly dissolves with development of heat, and then the whole sets to a semi-solid mass of colourless crystals of a tin double salt of the amine, before the

oxime has entered completely into solution. The mixture is kept at the ordinary temperature for about an hour, the solid collected, washed with a little fuming hydrochloric acid, and dried in a vacuum desiccator over sulphuric acid and soda-lime. It is not advisable to attempt to complete the reduction of the oxime by digesting the mixture on the water-bath, because a partial transformation of the amine into hydrindantin occurs. The dry product is readily soluble in water with the exception of a small quantity of unaltered oxime which is removed by filtration. In order to isolate diketohydrindamine, the yellow solution of the double salt is freed from tin by hydrogen sulphide, and the filtrate from the metallic sulphide, which rapidly turns red, neutralised with ammonium carbonate, when yellow, glistening crystals separate. These are collected, washed with aqueous hydrogen sulphide, and dried in a vacuum desiccator. These operations must be carried out as rapidly as possible, because the amine is extremely sensitive to the oxygen of the air, turning first brown and then blue. Even with the greatest care the product, after drying, was dark coloured. All attempts to purify the substance by crystallisation failed, deep blue solutions being produced on boiling it with water or alcohol. The amine is insoluble in chloroform, and on washing it with boiling chloroform until the filtrate is almost colourless, it is left behind as a yellow, crystalline substance. This, however, does not represent the pure diketohydrindamine as has been ascertained by analysis. The compound reduces ammoniacal silver solutions in the cold, Fehling's solution on slightly warming, and readily reacts with aromatic aldehydes to yield coloured condensation products, which are less stable than 4-benzylideneamino-1-phenyl-3-methylpyrazolone.

1 : 3-*Diketo-2-benzylidenehydrindamine*, $C_6H_4<\substack{CO\\CO}>CH{\cdot}N{:}CH{\cdot}C_6H_5$.

On mixing the amine with an excess of benzaldehyde, the whole soon sets to a semi-solid mass of orange needles, which are washed, first with alcohol, then with ether, until the filtrate is light yellow, and dried in a vacuum desiccator. The substance melts and decomposes at 196°:

0·2050 gave 0·5800 CO_2 and 0·0825 H_2O. C = 77·16; H = 4·46.
0·2225 „ 11 c.c. N_2 at 20° and 759 mm. N = 5·64.
$C_{16}H_{11}O_2N$ requires C = 77·10; H = 4·42; N = 5·62 per cent.

1 : 3-*Diketo-2-benzylidenehydrindamine* is sparingly soluble in ether or cold alcohol; it dissolves in boiling alcohol, but at the same time decomposes into the aldehyde and the amine, which latter is finally oxidised by the oxygen of the air to the analogue of

murexide. Owing to this transformation, the filtrate from the small quantity of orange needles, which on cooling separate from the alcoholic solution, turns deep blue. The substance is hydrolysed also by water, readily on boiling, but slowly at the ordinary temperature, and the odour of benzaldehyde is noticeable on exposing it to the air.

1 : 3-*Diketo*-2-*salicylidenehydrindamine*,

$$C_6H_4{<}{CO \atop CO}{>}CH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OH.$$

This compound is prepared from salicylaldehyde and diketohydrindamine in the same way as the former, and resembles it in its properties. It is orange, and melts and decomposes at 248—249°:

0·2247 gave 10·4 c.c. N_2 at 19° and 766 mm. N = 5·36.
$C_{16}H_{11}O_3N$ requires N = 5·28 per cent.

1 : 3-*Diketo*-2-*anisylidenehydrindamine*,

$$C_6H_4{<}{CO \atop CO}{>}CH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}O{\cdot}CH_3.$$

This is sparingly soluble in boiling alcohol, and, at the same time, partly decomposes; from the solution, on cooling, beautiful orange needles separate, which melt and decompose at 215—216°, whereas the dark brown filtrate turns deep blue on contact with the air:

0·1940 gave 0·5193 CO_2 and 0·0825 H_2O. C = 73·0; H = 4·72.
$C_{17}H_{13}O_3N$ requires C = 73·12; H = 4·65 per cent.

1 : 3-*Diketo*-2-p-*dimethylaminobenzylidenehydrindamine*,

$$C_6H_4{<}{CO \atop CO}{>}CH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}N(CH_3)_2$$

This compound is prepared by mixing an alcoholic solution of *p*-dimethylaminobenzaldehyde with diketohydrindamine; after a short time the whole sets to a mass of dark red needles, which are sparingly soluble in boiling alcohol, readily so in hot glacial acetic acid, and crystallise from these solvents in raspberry-coloured needles, melting and decomposing at 239°. The substance is more stable than those described above:

0·1605 gave 13·6 c.c. N_2 at 20° and 760 mm. N = 9·69.
$C_{18}H_{16}O_2N_2$ requires N = 9·59 per cent.

Diketohydrindylidenediketohydrindamine,

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>CH\cdot N\colon C<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4.$$

The ammonium salt of this substance, which is the analogue of murexide, is formed by the oxidation of diketohydrindamine or by the action of ammonium carbonate on hydrindantin. It is readily prepared according to the second method by following Piloty and Finckh's directions (*loc. cit.*) for the production of murexide. For this purpose a solution of ammonium acetate (13 grams) in water (50 c.c.) is neutralised with ammonia and mixed with a solution (5 c.c.) of ammonia (10 per cent.), which has been previously saturated with carbon dioxide; to the hot mixture of the ammonium salts, hydrindantin (2·5 grams), suspended in boiling water (250 c.c.), is gradually added with constant stirring, when a brown solid is produced. After about half an hour this is collected, and boiled with water. The dark blue filtrate from which, on cooling, only a small quantity of crystals with metallic lustre separates, is poured into a strong solution of ammonium chloride, when the organic ammonium salt is precipitated. It is washed with water until the filtrate is deep blue, and dried, first in a vacuum desiccator and then in the water-oven:

0·2020 gave 0·5010 CO_2 and 0·0690 H_2O. C = 67·64; H = 3·79.
0·2665 „ 20·4 c.c. N_2 at 18° and 759 mm. N = 8·82.
$C_{18}H_{12}O_4N_2$ requires C = 67·50; H = 3·75; N = 8·75 per cent.

On adding dilute hydrochloric acid to the cold blue solution of this salt, *diketohydrindylidenediketohydrindamine* is precipitated as a red powder with superficial metallic lustre. This must be collected at once, washed with water, and dried in a vacuum desiccator, because it is unstable in the presence of mineral acids, and gradually dissolves to yield a yellow solution:

0·2410 gave 10·2 c.c. N_2 at 21° and 770 mm. N = 4·88.
$C_{18}H_9O_4N$ requires N = 4·62 per cent.

This analogue of purpuric acid is readily decomposed by potassium hydroxide, as it is by mineral acids; it dissolves in dilute ammonia to form a blue solution of the ammonium salt. This reaction is so sensitive that it is possible by means of this substance to detect the traces of ammonia present in the distilled water of the laboratory.

Diketohydrindylideneuramil, $CO<\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}>CH\cdot N\colon C<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4.$

The potassium salt of this compound is prepared on proceeding as follows. Uramil (0·8 gram) is added to dilute potassium

hydroxide (containing 0·32 gram KHO) after having displaced the air by hydrogen. The solution which is gradually produced on warming, is poured into a solution of triketohydrindene hydrate (1 gram in 10 c.c.). The mixture turns reddish-violet, and in a short time clusters of small, brown needles separate. These are washed with water, and dried in a vacuum desiccator:

0·2570 gave 0·0683 K_2SO_4. K = 11·91.

0·2425 „ 27 c.c. N_2 at 21° and 773 mm. N = 12·89.

$C_{13}H_6O_5N_3K$ requires K = 12·07; N = 13·0 per cent.

The salt on ignition frothes considerably; it is therefore necessary to heat gradually in the determination of the metal. The potassium compound dissolves in water to yield a deep reddish-violet solution, which, on adding dilute hydrochloric acid, is decolorised immediately with the separation of uramil.

Action of Triketohydrindene Hydrate on Amino-acids.

As mentioned before (this vol., p. 793), the blue coloration which the triketone yields with amino-acids is accompanied by the formation of aldehydes, except in the case of glycine, which, on warming its aqueous solution with the reagent, does not yield formaldehyde. This fact corresponds with Strecker's observation (*loc. cit.*; see also Hurtley and Wootton, this vol., p. 288) of the behaviour of alloxan towards glycine. With regard to the other products which are formed in the reaction, it has so far been ascertained that the ammonium salt of diketohydrindylidenediketohydrindamine is produced, and that the colour test is based on the formation of this salt. This fact was established by examining the action of alanine on triketohydrindene hydrate. On mixing warm concentrated aqueous solutions of equal weights of the reagents, a deep blue solution is produced; at the same time acetaldehyde and carbon dioxide are formed, and a dark bluish-brown solid separates. After about half an hour, this is collected, and washed with a little water; it dissolves partly in boiling water, and the blue filtrate, when mixed with ammonium chloride, yields a reddish-brown precipitate. This was proved to be the analogue of murexide by analysis and by the transformation into the corresponding acid. The part which is insoluble in water has not yet been examined.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CLXXI.—*The Action of Ammonia and Amines on 2-Phenyl-1 : 3-benzoxazine-4-one.*

By Arthur Walsh Titherley and Ernest Chislett Hughes.

It has already been shown by one of the authors (Trans., 1910, **97**, 209) that 2-phenyl-1 : 3-benzoxazine-4-one (I) reacts with aniline readily with ring rupture, forming a yellow compound, salicylphenylbenzamidine. The addition of other amines and of ammonia has since been studied closely, and the observations are embodied in the present paper. It has been found that addition takes place with great readiness in all cases, and with ammonia, salicylbenzamidine (II) is formed, which crystallises in fine orange needles:

$$C_6H_4\!<\!\begin{matrix}CO\cdot N\\ \| \\ O-CPh\end{matrix} \xrightarrow{NH_3} C_6H_4\!<\!\begin{matrix}CO\cdot N\dot{:}CPh\\ \qquad\quad | \\ OH \quad NH_2\end{matrix}$$

(I.) (II.)

The constitution of the orange compound (II) has been confirmed by its independent synthesis from phenyl salicylate and benzamidine, thus:

$$OH\cdot C_6H_4\cdot CO_2Ph + CPh(\dot{:}NH)\cdot NH_2 \longrightarrow OH\cdot C_6H_4\cdot CO\cdot N\dot{:}CPh\cdot NH_2 + PhOH.$$

In this synthesis a compound, $C_{21}H_{15}ON_3$, which crystallises in pale yellow needles, is also formed by a secondary reaction. The constitution of this compound, which has previously been obtained by Pinner (*Ber.*, 1890, **23**, 2934, 3824) from ethyl salicylate and benzamidine, is discussed on p. 1499. The authors show that it is formed by the further action of benzamidine on salicylbenzamidine, which was not isolated by Pinner.

2-Phenyl-1 : 3-benzoxazine-4-one reacts with primary amines in a similar way to ammonia, yielding amidines which are yellow, and have a similar constitution. These amidine derivatives show varying degrees of stability, and while the simple amidine (II) is perfectly stable at 100°, the substituted amidines, $OH\cdot C_6H_4\cdot CO\cdot N\dot{:}CPh\cdot NHR$, at 90—100° lose the primary amine $R\cdot NH_2$ more or less readily, with production of the unsaturated cyclic compound (I). This has already been noted in the case of salicylphenylbenzamidine (*loc. cit.*), which readily dissociates at 100°. The methyl and ethyl derivatives (IV) obtained by the addition of methylamine or ethylamine to the cyclic compound (I) are much more thermostable than the phenyl derivative, but on long-continued heating in an open vessel at 100° they lose methylamine and ethylamine respectively, yielding 2-phenyl-1 : 3-benzoxazine-4-one (I). There can be little doubt that the unstable and hypothetical cyclic compound

(III) is intermediate, both in the synthetic formation and reversible decomposition in each case:

$$C_6H_4<\begin{matrix}CO\cdot N \\ O-CPh\end{matrix} \quad \underset{\longleftarrow}{\xrightarrow{R\cdot NH_2}} \quad C_6H_4<\begin{matrix}CO\cdot NH \\ O-CPh\cdot NHR\end{matrix} \quad \rightleftarrows$$
(I.) (III.)

$$C_6H_4<\begin{matrix}CO\cdot N:CPh\cdot NHR \\ OH\end{matrix}$$
(IV.)

and a similar mechanism holds in the case of the addition of ammonia, this view being supported by several considerations.

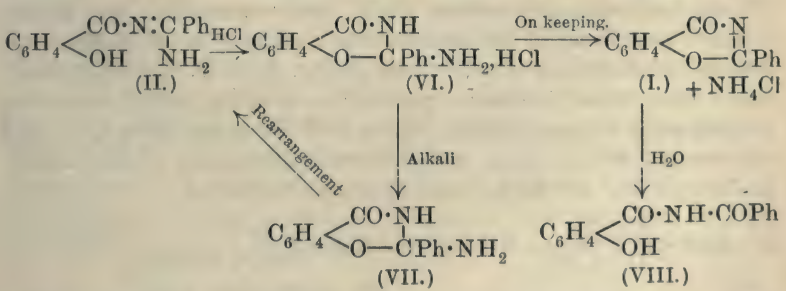
The open-chain amidine derivatives thus exhibit metoxazone tautomerism analogous to that observed among the acyl-salicylamides, in which the cyclic hydroxy-form, $C_6H_4<\begin{matrix}CO\cdot NH \\ O-CPh\cdot OH\end{matrix}$, is too unstable to exist in a free condition. They also exhibit ename-ketimine (amidine) tautomerism in the open-chain form, and in the case of salicylbenzamidine the tautomeric forms are:

$$OH\cdot C_6H_4\cdot CO\cdot N:CPh\cdot NH_2 \rightleftarrows OH\cdot C_6H_4\cdot CO\cdot NH\cdot CPh:NH.$$
(II.) (V.)

Owing to the bright yellow colour of salicylbenzamidine and its derivatives, and the interest attaching to their true constitution, a close study of their relations has been made, the outcome of which is to make it probable that the ename type of formula (II and IV) is the correct one for the pure solid substances. Their properties, however, including their peculiar behaviour with acids and alkali referred to below, make it impossible to assign the yellow colour to any single type of structure, and these properties seem to be consistent only with the supposition that the open-chain forms are verging on ring-formation, and that the colour is due to some oscillatory play of residual affinities between the hydroxylic and the amidine groupings. Their behaviour with acids may be best illustrated by considering the case of salicylbenzamidine (II). The orange needles, which show both phenolic and basic properties, are insoluble in ammonia, but dissolve in sodium hydroxide to a nearly colourless solution, from which by neutralisation with acids a pale yellow, apparently amorphous precipitate is produced; if rapidly treated with ammonia, this dissolves to a pale yellow solution. From the latter, orange needles of the original substance rapidly separate on keeping. The unstable acid form, soluble in ammonia, may possibly be the imino-compound (V), but it is not possible to isolate it owing to the rapidity with which it is transformed into the orange needles (II).

When the solution of the orange needles in alkali is treated with

excess of dilute hydrochloric acid, the yellow precipitate dissolves to a colourless solution, which in a short time deposits a mass of fine colourless needles, consisting of a hydrochloride sparingly soluble in hydrochloric acid. On careful treatment with alkali, the orange-coloured base may be recovered unchanged. The same colourless hydrochloride is obtained by the action of concentrated hydrochloric acid on a solution of the orange compound in acetone. The colour immediately disappears, and a mass of colourless, transparent crystals is deposited. The hydrochloride, freed from acid, on treatment with water, undergoes partial dissociation, giving the solid orange-yellow compound and a pale yellow solution, which on keeping soon becomes turbid, and deposits eventually a pale yellow jelly consisting of *N*-benzoylsalicylamide (white) in a nearly pure form. If water containing a trace of hydrochloric acid instead of pure water is used, the hydrochloride dissolves to a colourless solution, which soon deposits a perfectly white precipitate (microscopic needles) of *N*-benzoylsalicylamide, and the same substance is similarly obtained by the direct treatment of the free base, salicylbenzamidine in aqueous alcohol, with dilute hydrochloric acid. The decomposition is, under ordinary conditions, nearly complete in an hour. The colourless, unstable hydrochloride, for reasons advanced below, is believed to be the cyclic compound (VI), a salt of the cyclic amino-compound (VII), which, however, cannot exist in the free state, but immediately undergoes rearrangement into the orange compound (II). On this view the cyclic hydrochloride in faintly acid aqueous solution suffers gradual loss of ammonia as ammonium chloride, yielding 2-phenyl-1:3-benzoxazine-4-one (I), which, being extremely sensitive to hydrogen ions, immediately suffers hydrolytic fission, as previously shown by one of the authors (Trans., 1910, **97**, 209), yielding *N*-benzoylsalicylamide (VIII):



The alternative view that the colourless hydrochloride is a salt of the open-chain base (II) is discountenanced by a consideration of the properties of *o*-methoxybenzoylbenzamidine (X), in which the mobile phenolic hydrogen atom is replaced. This compound was

synthesised from phenyl *o*-methoxybenzoate (IX) by condensation with benzamidine, thus:

$$C_6H_4\!<\!\begin{matrix}CO_2Ph\\ OMe\end{matrix} + CPh(:NH)\cdot NH_2 \longrightarrow C_6H_4\!<\!\begin{matrix}CO\cdot N:CPh\cdot NH_2\\ OMe\end{matrix} + PhOH$$

(IX.) (X.)

The compound (X) is a quite colourless base, and its hydrochloride is practically unaffected in presence of aqueous hydrochloric acid in the cold. On heating, however, it is slowly converted into *N*-benzoyl-*o*-methoxybenzamide, identical with the compound obtained by McConnan and Titherley (Trans., 1906, **89**, 1332). This relatively difficult hydrolysis by hot acids is the normal decomposition of amidines, and is precisely similar to that which can be effected under similar conditions with benzoylbenzamidine, $C_6H_5\cdot CO\cdot N:CPh\cdot NH_2$, which yields dibenzamide. The easy hydrolysis of salicylbenzamidine in the cold, and the still more rapid acid hydrolysis of its derivatives of the type

$$OH\cdot C_6H_4\cdot CO\cdot N:CPh\cdot NHR,$$

which is complete in the cold in the course of a few minutes, stands out as a different type of reaction from ordinary amidine hydrolysis.

In order to throw further light on the constitution of salicylbenzamidine and its derivatives, the behaviour of 2-phenyl-1:3-benzoxazine-4-one with secondary amines was studied, and for this purpose dimethylamine, diethylamine, and diphenylamine were chosen. Considerable difficulty was experienced, inasmuch as although addition takes place at once in the cold in presence of solvents, mixtures of labile isomeric forms result, which on evaporating give yellow, difficultly crystallisable syrups. In the addition of dimethylamine, separation could not be effected, but with diethylamine a definite crystalline solid was obtained in colourless crystals. This compound from its properties must be 2-diethylamino-2-phenyl-dihydro-1:3-benzoxazine-4-one (XI), and represents the simple additive compound of the unsaturated cycloid (I). It is, however, extremely labile, and slowly turns yellow, even in the solid condition. In solvents, it gives a pale yellow solution, which shows the properties of an equilibrium mixture of the cyclic form (XI) and open-chain, yellow form, salicyldiethylbenzamidine (XII), which, however, could not be isolated in a pure condition:

$$C_6H_4\!<\!\begin{matrix}CO\cdot N\\ O-CPh\end{matrix} + NHEt_2 \longrightarrow C_6H_4\!<\!\begin{matrix}CO\cdot NH\\ O-CPh\cdot NEt_2\end{matrix} \rightleftarrows$$

(I.) (XI.) Colourless (m. p. 81°).

$$C_6H_4\!<\!\begin{matrix}CO\cdot N:CPh\cdot NEt_2\\ OH\end{matrix}$$

(XII.) Yellow (not isolated).

The colourless compound and yellow mixture dissolve at once in

dilute hydrochloric acid, forming a clear, colourless solution of the cyclic hydrochloride, which decomposes with great rapidity, in a similar manner to salicylbenzamidine. Diethylamine is eliminated, and a white precipitate of *N*-benzoylsalicylamide is produced. The extreme ease of this change, which is complete in the course of 5—6 seconds in the cold, confirms the supposition already expressed that in salicylbenzamidine (II) and all these derivatives the decomposition by acids is not simple amidine hydrolysis, and that acids produce salts of the (colourless) cyclic isomeric forms, which then more or less readily lose ammonia or amines, yielding the unsaturated cycloid (I); the latter, under the influence of acids, combines with water as it is formed, and by ring fission yields *N*-benzoylsalicylamide.

From these considerations it follows that in the majority of cases the stable existent form of these compounds in the free condition is the open-chain amidine form (as in II), which is yellow, whilst the hydrochlorides, which are colourless and more or less rapidly decomposed by water, possess the cyclic constitution, and are derivatives of dihydro-1:3-benzoxazine-4-one (as in VI). The only case observed where the stable form in the free condition possesses this cyclic structure is the diethylamino-derivative, which, however, rapidly comes into equilibrium with the yellow, open-chain amidine form in solution.

The addition of diphenylamine to 2-phenyl-1:3-benzoxazine-4-one (1) gave interesting results. In benzene solution the two combine, giving a deep yellow solution, which yields a syrupy mixture on evaporation. Difficulty was experienced owing to easy reversible dissociability of the additive compound into its constituents. When a hot solution of the unsaturated cyclic compound (I) in light petroleum was treated with an equivalent amount of diphenylamine, a colourless solution resulted, which became pale yellow on cooling. By keeping warm and adding an excess of diphenylamine (which is very soluble in light petroleum), the colour intensified as the increased mass of the diphenylamine increased the amount of the additive compound, until finally it separated out on cooling slightly as a mass of beautiful yellow needles. The constitution of this diphenylamine derivative presents some difficulty. Although its yellow colour, having regard to the above considerations, suggests the open-chain amidine structure (XIII), its insolubility in sodium

$$C_6H_4{<}^{CO\cdot N}_{O-CPh} + NHPh_2 \rightleftarrows C_6H_4{<}^{CO\cdot NH}_{O-CPh\cdot NPh_2} \rightleftarrows$$

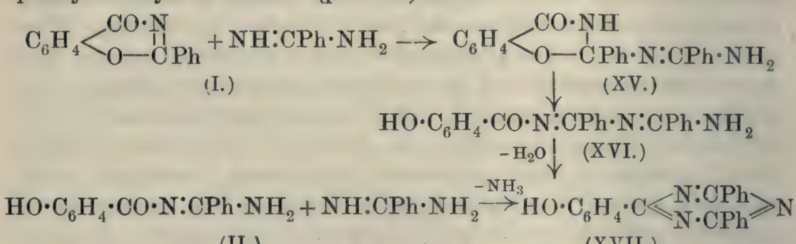
(XIV.)

$$C_6H_4{<}^{CO\cdot N:CPh\cdot NPh_2}_{OH}$$

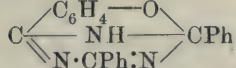
(XIII.)

hydroxide and the fact that it gives no coloration with ferric chloride suggests the cyclic formula (XIV), which is also consistent with its very easy dissociability.

The amidine formula (XIII) is believed by the authors to represent the true constitution of the compound, and the absence of phenolic properties is attributed to the powerful steric influence of the large amidine grouping carrying three phenyl radicles. It must, in fact, be supposed that although conventionally written as an open-chain system, it is one verging on ring-formation, and on this account, as well as on account of the magnitude of the groups in the critical position, the compound is virtually, so far as its properties are concerned, a cyclic compound, although there is a sufficient play of residual affinities in the open-chain form to produce colour. This disappearance of phenolic properties has been observed in another interesting case by the authors. When 2-phenyl-1:3-benzoxazine-4-one (I) in alcoholic solution is treated with benzamidine, a bright yellow solution results, evidently containing the complex amidine derivative (XVI). This, however, cannot be isolated owing to the remarkable tendency it has to undergo internal condensation, producing a compound $C_{21}H_{15}ON_3$, shown to be salicyldiphenylcyanidine (XVII), which rapidly separates out as a very pale yellow, crystalline powder, the yield being quantitative. The same compound (XVII) is produced, together with ammonia, by heating salicylbenzamidine and benzamidine together in alcoholic solution, and it is formed in this way as a by-product in the synthesis of salicylbenzamidine by the phenyl salicylate method (p. 1493):



The compound (XVII) is identical with that obtained by Pinner (*loc. cit.*), who, noting its insolubility in sodium hydroxide, gave it the formula:



Such a constitutional formula is not inconsistent with its synthesis from 2-phenyl-1:3-benzoxazine-4-one, since it could be derived by internal condensation from the intermediate additive

compound (XV), but it is difficult to reconcile with its easy production from salicylphenylbenzamidine (II), which has no tendency to lose ammonia. Moreover, the compound is, like cyaphenine (triphenylcyanidine), devoid of basic properties such as should be associated with Pinner's formula. Taking all the facts into account, the compound must be regarded as *o*-hydroxycyaphenine, and the suppression of ordinary phenolic properties must be attributed to the steric influences already referred to. That the phenolic properties are not entirely suppressed has been shown by the authors in the fact that, although the compound gives no ferric chloride reaction and is not affected by aqueous sodium hydroxide, it yields with sodium ethoxide in alcohol a bright yellow sodium derivative, which is decomposed by excess of water with production of the unchanged compound.

A similar case of disappearance of phenolic properties has been lately observed by Torrey and Adams (*Ber.*, 1910, **43**, 3227) in certain hydrazone derivatives of pæonol like

$$MeO\cdot C_6H_3(OH)\cdot CMe{:}N\cdot NH\cdot C_6H_4\cdot NO_2,$$

which is not affected by alkali. The position of the hydroxyl group is similar in these derivatives to those of the authors.

Experimental.

Salicylbenzamidine, $OH\cdot C_6H_4\cdot CO\cdot N{:}CPh\cdot NH_2$.

(1) *Preparation from 2-Phenyl-*1:3-*benzoxazine*-4-*one*.—Twenty grams of 2-phenyl-1:3-benzoxazine-4-one dissolved in 200 c.c. alcohol were saturated with gaseous ammonia, and the bright yellow solution was allowed to evaporate. Salicylbenzamidine (20 grams) separated as a mass of practically pure, transparent, orange-yellow needles. By recrystallisation from a mixture of benzene and light petroleum (1:3), the compound was obtained in silky, orange needles, melting at 136°.

An alternative method of preparation consisted in treating the alcoholic solution of 2-phenyl-1:3-benzoxazine-4-one with concentrated aqueous ammonia, when, after half an hour, salicylbenzamidine separates as a mass of orange needles in nearly quantitative yield:

0·1669 gave 17·3 c.c. N_2 at 23° and 743 mm. N = 11·42.

$C_{14}H_{12}O_2N_2$ requires N = 11·66 per cent.

(2) *Preparation from Phenyl Salicylate*.—Two grams of phenyl salicylate were mixed with 1 gram of benzamidine, freshly prepared from its hydrochloride, when an immediate reaction took place with evolution of heat. A yellow colour developed, and a mass of nearly white crystals, probably the phenyl salicylate salt of benzamidine,

were deposited. About 20 c.c. of alcohol were now added, and the mixture heated to the boiling point. A rapid reaction took place with formation of a clear, bright yellow solution, from which in a few moments a mass of nearly colourless, short, silky needles separated (0·15 gram). These melted at 248°, and consisted of *o*-hydroxytriphenylcyanidine (p. 1498). (Found, N = 12·69. Calc., N = 12·90 per cent.)

The alcoholic filtrate on careful dilution with water gave salicylbenzamidine as a mass of orange-yellow needles (0·8 gram), melting, after recrystallisation from a mixture of benzene and light petroleum, at 136—137°:

0·2889 gave 28·3 c.c. N_2 at 17° and 764 mm. N = 11·43.

$C_{14}H_{12}O_2N_2$ requires N = 11·66 per cent.

Salicylbenzamidine is readily soluble in alcohol, acetone, or chloroform, moderately so in ether or benzene, and practically insoluble in light petroleum. Its solution in acetone gives an intense purple-red colour with alcoholic ferric chloride. It is immediately soluble in dilute sodium hydroxide to a very pale yellow solution, which with dilute hydrochloric acid gives a yellow precipitate, which at once dissolves in excess of acid. The resulting colourless solution, after one minute, deposits a thick mass of fine white needles, consisting of a hydrochloride insoluble in hydrochloric acid. The hydrochloride on keeping soon changes to *N*-benzoylsalicylamide. Even if it is rapidly collected this decomposition cannot be avoided, and on washing the precipitate it becomes pale yellow, owing to partial dissociation. The pure *hydrochloride* was obtained by treating a solution of 1 gram of salicylbenzamidine in 15 c.c. of acetone with 1 c.c. of concentrated hydrochloric acid. It separated after a short time as a mass of small, colourless needles (1·25 grams), which were washed with acetone and dried in a vacuum, in which, however, slight dissociation occurred, and a slightly yellow colour developed. It was analysed by decomposition with water containing a small quantity of nitric acid. The *N*-benzoylsalicylamide formed was weighed, and the hydrochloric acid determined by titration:

0·2078 gave 0·1650 *N*-benzoylsalicylamide (theory 0·1810) and required 7·1 c.c. $N/10$-$AgNO_3$. Cl = 12·13.

$C_{14}H_{12}O_2N_2,HCl$ requires Cl = 12·8 per cent.

The hydrochloride on heating to 120° partly melted, and lost ammonium chloride, giving 2-phenyl-1:3-benzoxazine-4-one, which was isolated by extraction with benzene, washing the benzene solution with alkali, and evaporating. After recrystallisation from light petroleum, it melted at 106°, and gave the characteristic reaction with hydrochloric acid (Trans., 1910, **97**, 207).

The hydrochloride dissolves fairly readily in alcohol with slight dissociation and a faint yellow colour. This solution gives a port-wine tint with alcoholic ferric chloride, but if previously treated with very dilute alcoholic hydrogen chloride until just colourless the solution gives no ferric chloride coloration.

The hydrochloride is partly dissociated by water, forming a pale yellow solution, and generally leaving a little free base insoluble as a yellow solid, but a colourless solution results if a small quantity of free hydrochloric acid is added. The pale yellow aqueous solution on being kept for a few minutes deposits pale yellow needles (m. p. 132°) of salicylbenzamidine, and later a sulphur-yellow precipitate, consisting of a mixture of this and *N*-benzoylsalicylamide. The acidified colourless solution on keeping deposits continually a white precipitate of pure *N*-benzoylsalicylamide (m. p. 208°). The decomposition is nearly complete in an hour at the ordinary temperature, as shown in the curve on p. 1508; at higher temperatures it is practically instantaneous.

Salicylmethylbenzamidine, $OH \cdot C_6H_4 \cdot CO \cdot N:CPh \cdot NHMe$.

One gram of 2-phenyl-1:3-benzoxazine-4-one in saturated alcoholic solution was treated with 0·45 gram of a 33 per cent. aqueous solution of methylamine. A yellow colour was immediately produced, and after some time salicylmethylbenzamidine separated in large, yellow, hexagonal plates, leaving a yellow syrup. After washing with dilute alcohol and recrystallising from light petroleum, it was obtained in bundles of yellow needles, melting at 95°:

0·6332, by Kjeldahl's method, required 50·0 c.c. *N*/10-HCl. N = 11·06.

$C_{15}H_{14}O_2N_2$ requires N = 11·03 per cent.

Salicylmethylbenzamidine is fairly soluble in the cold in alcohol or ether, and readily so in acetone or benzene. It is easily soluble in all hot solvents. It gives a strong red coloration with ferric chloride. On heating at 90—100°, it gradually loses methylamine, and leaves 2-phenyl-1:3-benzoxazine-4-one, the yield of which on small quantities is nearly theoretical in six days (0·1270 gave 0·1130; theory requires 0·1115). Salicylmethylbenzamidine dissolves in sodium hydroxide to a very pale yellow solution, and in dilute hydrochloric acid to a colourless solution, from which *N*-benzoylsalicylamide is rapidly deposited, the decomposition being practically complete at 15° in about fifteen minutes.

Salicylethylbenzamidine, $OH\cdot C_6H_4\cdot CO\cdot N\!:\!CPh\cdot NHEt$.

A saturated alcoholic solution of 3 grams of 2-phenyl-1:3-benzoxazine-4-one was treated with 3 grams of 33 per cent. aqueous ethylamine. A yellow colour was produced immediately, and in a short time yellow needles of salicylethylbenzamidine formed, which were collected after three hours. The yield was 2 grams, and the compound, after recrystallising from light petroleum, melted at 118—119°:

0·4824, by Kjeldahl's method, required 35·5 c.c. *N*/10-HCl. N = 10·30.

$C_{16}H_{16}O_2N_2$ requires N = 10·45 per cent.

Salicylethylbenzamidine is very sparingly soluble in cold ether or light petroleum, readily so in cold acetone or benzene, and moderately so in cold alcohol. When heated at 90—100° it slowly loses ethylamine, leaving 2-phenyl-1:3-benzoxazine-4-one (m. p. 106°), the decomposition being complete in six days. (0·1340 gave 0·1120, theory requires 0·1115.) Salicylethylbenzamidine gives a deep red coloration with ferric chloride; it dissolves in sodium hydroxide to a very pale yellow solution, and in dilute hydrochloric acid to a colourless solution, from which *N*-benzoylsalicylamide is rapidly deposited, the decomposition being practically complete at 15° in five minutes.

Action of Dimethylamine on 2-Phenyl-1:3-benzoxazine-4-one.

The interaction between these substances was tried under a variety of conditions, using ether, alcohol, benzene, and light petroleum as solvents, and in each case yellow solutions were obtained, which on evaporation left viscid, yellow syrups. The latter evidently consisted of a mixture of salicyldimethylbenzamidine and 2-dimethylamino-2-phenyldihydro-1:3-benzoxazine-4-one, and on keeping in a vacuum for several weeks partly crystallised, but owing to the tendency which these two compounds have to suffer rearrangement, forming an equilibrium mixture, it was found impossible to effect a proper separation. The crystals, which were obtained only in very small quantity, melted at temperatures between 90° and 106°. A determination of nitrogen in the syrupy mixture was made:

0·2244, by Kjeldahl's method, required 16·8 c.c. *N*/10-HCl. N = 10·48.

$C_{16}H_{16}O_2N_2$ requires N = 10·45 per cent.

The mixture gave a deep reddish-violet colour with ferric chloride, and was rapidly decomposed by dilute hydrochloric acid, yielding dimethylamine and *N*-benzoylsalicylamide.

Action of Diethylamine on 2-Phenyl-1:3-benzoxazine-4-one.

2-Diethylamino-2-phenyldihydro-1:3-benzoxazine-4-one,

$$C_6H_4<\begin{matrix}CO\cdot NH\\ O-CPh\cdot NEt_2\end{matrix}.$$

—Similar difficulties were encountered to those mentioned in the case of dimethylamine, but after several trials one of the two products formed (the cyclic diethyl derivative) was definitely isolated as follows: Five grams of 2-phenyl-1:3-benzoxazine-4-one in 50 c.c. of pure benzene were treated with a solution of 1·5 grams of diethylamine in benzene. A yellow colour rapidly developed, and on evaporation at 15° a yellow syrup was left, which in a few days set to a crystalline mass. The solid consisted essentially of the cyclic base, and after draining weighed 5·5 grams. By careful treatment with cold 5 per cent. aqueous sodium hydroxide, the isomeric yellow salicyldiethylbenzamidine present was removed, leaving a white solid (5 grams). Attempts to obtain salicyldiethylbenzamidine from the alkaline filtrate by cautious treatment with acetic acid or carbon dioxide gave only *N*-benzoylsalicylamide, diethylamine being eliminated. The solid remaining after treatment with alkali was recrystallised by dissolving in alcohol at 40°, and cautiously adding water; on keeping, pure 2-diethylamino-2-phenyldihydro-1:3-benzoxazine-4-one separated in colourless needles, melting at 81°, and weighing 3 grams:

0·4124, by Kjeldahl's method, required 27·0 c.c. *N*/10-HCl. N = 9·17.

$C_{18}H_{20}O_2N_2$ requires N = 9·46 per cent.

The cyclic base undergoes partial rearrangement to the yellow open-chain isomeride, even in the solid condition, and the change can be traced in the yellow colour which the colourless crystals acquire on keeping a few hours. The tautomeric change appears to be practically instantaneous in solution. The compound dissolves easily in cold benzene, acetone, or chloroform to pale yellow solutions, which leave a syrupy mixture of the two isomerides on spontaneous evaporation. In carbon tetrachloride and ethyl acetate, in which the compound is readily soluble, and in alcohol, in which it is moderately soluble, the yellow colour is only very slight, and the equilibrium between the colourless ring and yellow open-chain isomerides is clearly dependent on the nature of the solvent. The solutions in alcohol and acetone give a reddish-violet colour with ferric chloride. The cyclic base, like salicylmethylbenzamidine and salicylethylbenzamidine, readily dissociates on heating to about 90°. Diethylamine is lost, and after heating for fifteen hours the liquid sets to a crystalline mass of 2-phenyl-1:3-benz-

oxazine-4-one, melting at 103°. The behaviour of the compound with hydrochloric acid was studied in order to throw light on the action of hydrochloric acid on salicylbenzamidine (p. 1500). The cyclic base dissolves readily in excess of cold dilute hydrochloric acid to a colourless solution, which, if the solution is not too dilute, in a few seconds deposits a white, microcrystalline precipitate of the hydrochloride. The latter on warming with aqueous ammonia dissolves to a bright yellow solution, which on cooling deposits a mass of needles of salicylbenzamidine, melting at 135°. 2-Phenyl-1:3-benzoxazine-4-one is undoubtedly first produced, and then combines with ammonia, and the same mechanism explains the ready decomposition of the hydrochloride with water. When the cyclic base in a finely divided state is suspended in sufficient water (to prevent the hydrochloride being precipitated), on adding dilute hydrochloric acid a clear solution is formed, but hydrolysis rapidly takes place, and an abundant precipitate of *N*-benzoylsalicylamide (m. p. 200°) begins to be deposited in about five seconds. By collecting at short intervals it was found that the decomposition (with formation of diethylamine) was practically complete in three minutes. The hydrochloride of the cyclic base is therefore very much more rapidly hydrolysed than that of 2-amino-2-phenyl-dihydro-1:3-benzoxazine-4-one (p. 1501).

The pure *hydrochloride* was obtained by treating a solution of 2 grams of the cyclic base in benzene solution with dry hydrogen chloride:

0·0740 required 2·15 c.c. $N/10$-$AgNO_3$. Cl = 10·31.

$C_{18}H_{21}O_2N_2Cl$ requires Cl = 10·38 per cent.

The hydrochloride rapidly decomposes in moist air, and after twenty-four hours contained only 5·61 per cent. of chlorine. At the end of three weeks the remaining white solid consisted almost entirely of *N*-benzoylsalicylamide.

Action of Diphenylamine on 2-Phenyl-1:3-benzoxazine-4-one.

Salicyldiphenylbenzamidine, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}N{:}CPh{\cdot}NPh_2$. — A solution of 2·3 grams of 2-phenyl-1:3-benzoxazine-4-one in dry benzene was treated with a benzene solution of 1·7 grams of diphenylamine. A bright yellow colour was produced at once, and on allowing to evaporate, a syrup remained, which slowly crystallised. After draining and recrystallising from benzene, *salicyldiphenylbenzamidine* was obtained as a bright yellow, crystalline powder, melting at 92°:

0·6012, by Kjeldahl's method, required 30·1 c.c. $N/10$-HCl. N = 7·01.

$C_{26}H_{20}O_2N_2$ requires N = 6·98 per cent.

The compound gives no reaction with ferric chloride, and is insoluble in sodium hydroxide.

It is sparingly soluble in cold light petroleum, moderately so in cold alcohol or ether, and readily so in cold acetone or benzene, giving yellow solutions in each case. The yellow colour is not lost in hot alcohol, but it disappears in excess of hot benzene or light petroleum, and reappears on cooling, owing to the ready dissociation of the compound into 2-phenyl-1 : 3-benzoxazine-4-one and diphenylamine. The former can, in fact, be isolated from the hot light petroleum solution, if not too dilute, by cooling. An alternative method of preparation consisted in adding an excess of diphenylamine to a hot solution of 2-phenyl-1 : 3-benzoxazine-4-one in light petroleum, and allowing to cool, when the compound separated in bright yellow, silky needles melting at 92°

Action of Piperidine on 2-Phenyl-1 : 3-benzoxazine-4-one.

A yellow syrup only could be obtained, consisting apparently of open-chain and cyclic isomerides, which could not be separated. The syrup was easily soluble in benzene and acetone, and was practically insoluble in alkali. With acids, it yielded *N*-benzoylsalicylamide.

o-*Methoxybenzoylbenzamidine*, $MeO \cdot C_6H_4 \cdot CO \cdot N \colon CPh \cdot NH_2$.

The object in synthesising this compound was to compare its properties with those of salicylbenzamidine, and its synthesis was effected from benzamidine and phenyl *o*-methoxybenzoate, which was obtained from *o*-methoxybenzoic acid by a modification of the method described by Seifert (*J. pr. Chem.*, 1844, [ii], **31**, 474). *o*-Methoxybenzoic acid has been obtained by several methods (Cahour, *Annalen*, 1854, **92**, 315; Graebe, *Annalen*, 1866, **139**, 137; Graebe and Ullmann, *Ber.*, 1896, **29**, 825; Bromwell, *Amer. Chem. J.*, 1898, **19**, 577; Weida, *Amer. Chem. J.*, 1898, **19**, 552; Lander, Trans., 1900, **77**, 745), but as on trial these methods gave unsatisfactory yields it was prepared by the authors from salicylamide by methylation and subsequent hydrolysis as follows:

o-*Methoxybenzamide.*—Thirty grams of salicylamide in 200 c.c. alcohol were treated with a solution of 4·6 grams of sodium in 50 grams of alcohol, and then with 40 grams of methyl iodide. After boiling for an hour and a-half and distilling off most of the alcohol, *o*-methoxybenzamide was precipitated with water. It was purified by digesting with sodium hydroxide and recrystallising from hot water (yield 25 grams, m. p. 128°).

o-*Methoxybenzoic Acid.*—Twenty-five grams of *o*-methoxybenz-

amide were boiled with 60 c.c. of 10 per cent. sodium hydroxide for forty-five minutes, when the hydrolysis was complete. On cooling, diluting with water, and acidifying, *o*-methoxybenzoic acid was precipitated, and recrystallised from hot water (yield 18 grams, m. p. 93°).

Phenyl o-Methoxybenzoate.—Fifteen grams of *o*-methoxybenzoic acid mixed with 15 grams of freshly distilled phosphoryl chloride were treated at 75° with 9 grams of phenol, and the whole kept at 75° for four hours. The resulting red liquid after cooling was treated with water and shaken with 10 per cent. sodium hydroxide, and the insoluble oil extracted with ether. On evaporation a red oil remained, which solidified on stirring with a little dilute sodium hydroxide. The solid phenyl *o*-methoxybenzoate was purified by recrystallising first from aqueous alcohol and finally from pure alcohol, from which it separated in colourless, six-sided prisms, weighing 17 grams, and melting at 59°.

Condensation of Phenyl o-Methoxybenzoate and Benzamidine.—Five grams of phenyl *o*-methoxybenzoate in 10 c.c. of alcohol were treated with 6 grams of benzamidine, and the mixture heated to 50° for ten minutes. On cooling and adding water, *o*-methoxybenzoyl benzamidine (8 grams) was precipitated as a mass of colourless needles, which, after recrystallising from a little alcohol, melted at 128°:

0·2386, by Kjeldahl's method, required 18·7 c.c. *N*/10-HCl. N = 10·97.

$C_{15}H_{14}O_2N_2$ requires N = 11·02 per cent.

o-Methoxybenzoylbenzamidine is moderately soluble in cold alcohol, ether, or benzene, and readily so in acetone. It dissolves at once in dilute hydrochloric acid, forming a clear solution, which is only very slowly decomposed at 15°, but at 50° begins after half an hour to deposit *N*-benzoyl-*o*-methoxybenzamide in long needles. (Found: N = 5·76. Calc., N = 5·50 per cent.) The stability of the hydrochloride in presence of dilute hydrochloric acid was compared with that of salicylbenzamidine and benzoylbenzamidine, NBz:CPh·NH_2.

The latter compound, which has been described by Pinner (*Ber.*, 1878, **11**, 764; 1889, **22**, 1606) and by Beckmann and Sandel (*Annalen*, 1897, **296**, 285), was prepared by the authors by the condensation of phenyl benzoate (10 grams) and benzamidine (7·2 grams), which were heated at 50° for three hours. On cooling and adding water, an oil was precipitated, which was treated with dilute hydrochloric acid to separate the benzoylbenzamidine, which dissolved, from unchanged phenyl benzoate (1·5 grams). The acid filtrate on treatment with alkali gave the base as an oil, which

rapidly solidified (7 grams). After recrystallisation from light petroleum it was obtained in fine colourless needles, melting at 98°. In comparing the relative stability of the three amidines towards hydrochloric acid, attempts were made to carry out the measurements under strictly similar conditions, but whilst this is possible as between benzoylbenzamidine and *o*-methoxybenzoylbenzamidine, which are only very slowly decomposed, giving dibenzamide and *N*-benzoyl-*o*-methoxybenzamide respectively, in the case of salicylbenzamidine the hydrolysis is too rapid. Further, owing to the slight solubility in hydrochloric acid of the cyclic hydrochloride resulting from the latter, more water was necessary than can be used in the case of the first two amidines, since the basis of the measurements depended on weighing the resulting secondary amides, which are appreciably soluble in water; the secondary amide derived from salicylbenzamidine, however (*N*-benzoylsalicylamide), is extremely insoluble in water, excess of which does not therefore vitiate the results. The first experiments give a comparison between benzoylbenzamidine and *o*-methoxybenzoylbenzamidine. Two portions of 0·5 gram in each case were dissolved in 10 c.c. of 10 per cent. hydrochloric acid, and the resulting clear solutions allowed to remain (1) at 15°, and (2) at 40°. The crystalline secondary amide produced by hydrolysis was weighed after twenty-four hours in (1), and at intervals in (2), the readings being shown in Fig. 1.

Benzoylbenzamidine (0·5 gram).

	Temp.	Time.	Weight of dibenzamide.	Percentage hydrolysed.
(1).	15°	24 hours	0·13 gram	25·8

o-Methoxybenzoylbenzamidine (0·5 gram).

Temp.	Time.	Weight of *N*-benzoyl-*o*-methoxybenzamide	Percentage hydrolysed.
15°	24 hours	0·03 gram	5·9

In the second group of experiments salicylbenzamidine was treated with the same volume of dilute hydrochloric acid, containing one, two, and three molecular equivalents of hydrogen chloride respectively. 0·2 Gram of the substance was dissolved in (i) 8·4 c.c. of $N/10$-hydrochloric acid and 16·8 c.c. of water; (2) 16·8 c.c. of $N/10$-hydrochloric acid and 8·4 c.c. of water; and (3) in 25·2 c.c. of $N/10$-hydrochloric acid. At higher concentrations than these it is impossible to prevent the insoluble hydrochloride being precipitated. The temperature was kept at 15°, and the insoluble *N*-benzoylsalicylamide which continually separated out, was collected at intervals, dried, and weighed. The results are expressed in Fig. 2.

(2).

FIG. 1.

I. *Benzoyl benzamidine* (0·5 *gram*) *at* 40°.
II. o-*Methoxybenzoylbenzamidine* (0·5 *gram*) *at* 40°.

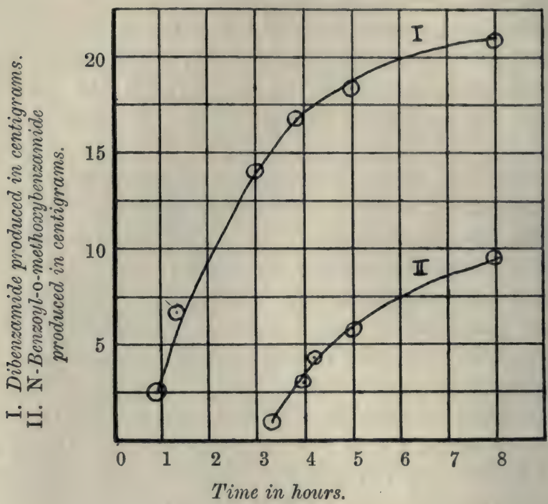
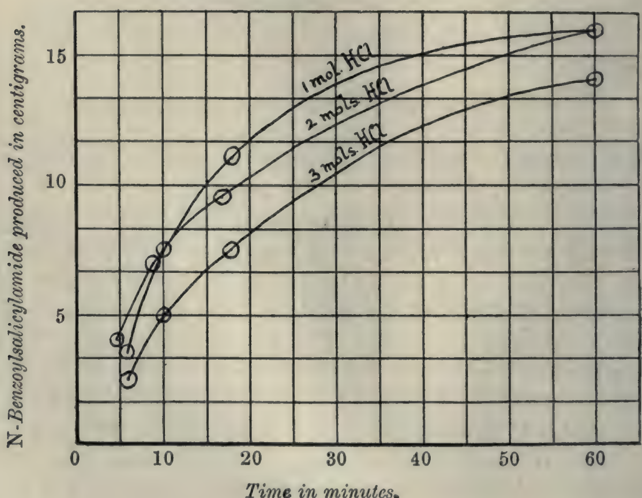


FIG. 2.

Salicylbenzamidine (0·2 *gram*) *at* 15°.



From a comparison of these curves, although the conditions are not the same, it is evident that the velocity of hydrolysis of salicylbenzamidine is vastly greater than that of the other two amidines, even at a higher temperature. It is noteworthy that of the two latter, *o*-methoxybenzoylbenzamidine is hydrolysed much more slowly than benzoylbenzamidine, and this is probably due to steric hindrance. The results in any case are only approximate, since molecular quantities were not taken, and owing to the error due to the slight solubility in water and supersaturation tendency of dibenzamide and *N*-benzoyl-*o*-methoxybenzamide. An unexpected feature in the case of salicylbenzamidine is the slightly inhibitory effect of excess of hydrochloric acid, which appears to increase the stability of the hydrochloride. This effect is probably connected with the fact, previously referred to, that in stronger solutions the hydrochloride is precipitated as a crystalline solid by excess of hydrochloric acid. The reverse effect would be expected if the decomposition were true hydrolysis, and increase in the concentration of the acid catalyst would cause corresponding increase in the velocity of hydrolysis. As it appeared therefore that the mechanism of decomposition was one in which ammonia was eliminated from the cyclic hydrochloride, yielding 2-phenyl-1 : 3-benzoxazine-4-one as the first product, it appeared to be desirable to examine the velocity of addition of water to this compound (producing *N*-benzoylsalicylamide) under the influence of varying quantities of hydrochloric acid. Alcoholic solutions of 2-phenyl-1 : 3-benzoxazine-4-one diluted with water to incipient turbidity were treated with the acid, and the resulting precipitate collected at intervals, but it was found that in all cases the velocity was so great that proper measurements could not be made. With one molecular equivalent of dilute alcoholic hydrochloric acid at $N/40$-concentration, the reaction is practically complete in sixty seconds. With $1/45$ of the molecular equivalent of acid at $N/3000$-concentration the reaction is complete in eight minutes. As the velocity of decomposition is greater than that of salicylbenzamidine and its derivatives, it would appear that the rate of decomposition of the latter by hydrochloric acid is controlled by the rate at which ammonia or amines are eliminated from their cyclic hydrochlorides.

Condensation of (1) *2-Phenyl-*1 : 3-*benzoxazine-*4-*one, and* (2) *Salicylbenzamidine, with Benzamidine.*

o-Hydroxytriphenylcyanidine, $HO\cdot C_6H_4\cdot C\leqslant\begin{matrix}N\colon CPh\\ N\cdot CPh\end{matrix}\geqslant N$. —This compound, under another constitutional formula, has already been described by Pinner (*loc. cit.*).

(1) A saturated alcoholic solution of 4·6 grams of 2-phenyl-1:3-benzoxazine-4-one was treated with an alcoholic solution of 2 grams of benzamidine freshly prepared from 2·8 grams of the hydrochloride. An immediate yellow colour was produced, which in the course of a few seconds gave place to a pale yellow, microcrystalline precipitate of pure *o*-hydroxytriphenylcyanidine. After washing with alcohol, it weighed 6·2 grams, and melted at 245°. A further small quantity was obtained from the filtrate on keeping. (Found: N=13·00. Calc., N=12·92 per cent.)

(2) A saturated alcoholic solution of 1 gram of salicylbenzamidine was heated with 0·35 gram of benzamidine for several hours. The cyanidine derivative slowly separated from the hot solution as a pale yellow solid in a practically pure form (0·3 gram). It was identical in all respects with that prepared by method (1) and with the by-product (p. 1500) obtained in the condensation between benzamidine and phenylsalicylate.

The compound does not show normal phenolic properties. Attempts to methylate it by diazomethane and to acetylate it by acetic anhydride and pyridine failed entirely. On treating with sodium ethoxide in alcohol, however, a bright yellow sodium salt was obtained, which was completely decomposed by water, forming the original compound.

Organic Laboratory,
University of Liverpool.

CLXXII.—*Optically Active Derivatives of* 1-*Methyl*cyclo*hexylidene*-4-*acetic Acid*.

By William Henry Perkin, jun., and William Jackson Pope.

During recent years we have described the preparation (Perkin and Pope, Trans., 1908, **93**, 1075) and resolution into optically active components (Perkin, Pope, and Wallach, Trans., 1909, **95**, 1789) of 1-methyl*cyclo*hexylidene-4-acetic acid,

$$\begin{matrix}CH_3\\H\end{matrix}\!\!>C<\!\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!\!>C:CH\cdot CO_2H,$$

a substance which, although its molecule contains no asymmetric atom, is nevertheless resolvable into components exhibiting optical activity in solution.

We have indicated that the optical activity is due to the enantiomorphous configuration of the molecule as a whole, and that this

kind of enantiomorphism cannot be distinguished by the location of an asymmetric atom in the molecule. The discovery of the new type of optically active substances referred to involves a considerable extension of the whole subject of stereochemistry; it is hence not surprising that our statement that the acid referred to above contains no asymmetric carbon atom in its molecule should have been contested.

The most ample criticism of our results has been published by Everest (*Chem. News*, 1909, **100**, 295), whose attitude is summarised in the following extract from his paper. He observes that "it appears doubtful whether the carbon atom (1) is not asym-

$$\begin{matrix}(b) & \overset{(9)}{\mathrm{CH_3}} \\ (a) & \mathrm{H}\end{matrix} > \underset{(1)}{\mathrm{C}} < \begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix} > \underset{(4)}{\mathrm{C}} = \underset{(7)}{\mathrm{C}} < \begin{matrix}\mathrm{H} & (c)\\ \mathrm{CO_2H} & (d)\end{matrix}$$

metric, and thus the cause of the optical activity. For beyond the hydrogen atom (*a*) and the methyl group (*b*) the configuration of the remainder of the molecule must be considered in order to decide the question, and it is here that I think the authors assume too much when they take it *that the configuration of the remainder of the molecule is the same when taken either way, relative to the carbon atom* (1); for such is assumed if the carbon atom (1) is said not to be asymmetric."

That this criticism will not withstand examination will be made clear by the following three remarks. (*a*) An asymmetric atom is never the cause of optical activity; optical activity is apparently invariably, and asymmetry of a carbon atom is in special cases, the result of enantiomorphism of molecular configuration. Optical activity and the presence in the molecule of an asymmetric atom cannot be considered as mutually related in the sense of cause and effect. (*b*) We have never made the assumption stated in the italicised portion of the above quotation, and have indeed indicated quite clearly (Trans., 1909, **95**, 1792) the erroneous nature of such an assumption. The consideration of a few simple molecular models will show that in any substance of enantiomorphous molecular configuration, the aspect of the arrangement, viewed from any component atom, is always enantiomorphous. (*c*) If Everest's view that a carbon atom is non-asymmetric only when "the configuration of the remainder of the molecule is the same when taken either way, relative to the carbon atom," is accepted, every atom, carbon, oxygen, or hydrogen, in the molecule of 1-methyl*cyclo*hexylidene-4-acetic acid—and indeed of any optically active substance—is asymmetric.

It must thus be granted that our original conclusion stands, and that in 1-methyl*cyclo*hexylidene-4-acetic acid we have realised for

the first time the existence of the most general type of enantiomorphism of molecular configuration foreseen by van't Hoff, a type which gives rise to optical activity, but in which no asymmetric atom can be distinguished.

In order to discriminate between this new type of enantiomorphous compound and those substances in which the enantiomorphism of molecular configuration is associated with the presence of an asymmetric carbon, nitrogen, or other atom in the molecule, it is convenient to introduce a special term; we shall refer to such substances as "centroasymmetric." A second example of the centroasymmetric optical activity has been recently described by Mills and Bain (Trans., 1910, **97**, 1866) in the oxime of *cyclo*-hexanone-4-carboxylic acid, $\begin{smallmatrix}CO_2H\\H\end{smallmatrix}{>}C{<}\begin{smallmatrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{smallmatrix}{>}C{:}N\cdot OH$.

The discovery of the new type of optical activity leads to the enunciation of a stereochemical problem which has never before presented itself, namely, the question as to what will occur when an optically active substance of which the enantiomorphism of molecular configuration is associated with one particular type of asymmetry is converted into a second substance of which the optical activity arises from the exhibition by the molecule of enantiomorphism of a quite different type. With the aid of the optically active 1-methyl*cyclo*hexylidene-4-acetic acids, it is possible to study the mode in which the optical activity is affected when the centroasymmetric substance is converted into, or is produced from, one containing an asymmetric carbon atom; the examination of these cases is of considerable interest in connexion with the mechanism of chemical change, and we have therefore investigated a number of such reactions.

Reduction of dl-, d-, *and* l-1-*Methyl*cyclo*hexylidene*-4-*acetic Acids.*

As a preliminary to studying the conversion of the optically active 1-methyl*cyclo*hexylidene-4-acetic acids into other potentially optically active substances, it seemed desirable to check the anticipations from theory in connexion with some more simple cases, those, namely, in which the centroasymmetric compounds are converted into others which should be potentially optically inactive. The reduction of 1-methyl*cyclo*hexylidene-4-acetic acid to the 1-methyl*cyclo*hexyl-4-acetic acid, $CHMe{<}\begin{smallmatrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{smallmatrix}{>}CH\cdot CH_2\cdot CO_2H$, would be expected to destroy the enantiomorphism of molecular configuration, and in accordance with this anticipation it is found that the reduction products of the optically active centroasymmetric acids are optically inactive.

dl-1-Methyl*cyclo*hexylidene-4-acetic acid is readily and completely

reduced when treated with hydrogen under the conditions described by A. Shika (*Ber.*, 1909, **42**, 1630). Gum arabic (30 c.c. of a 25 per cent. aqueous solution) is mixed with warm water (80 c.c.), 0·5 gram of palladous chloride in aqueous solution added, and, after mixing with a solution of the unsaturated acid (10 grams) in methyl alcohol (100 c.c.), the whole is transferred to a long, narrow cylinder, and a rapid stream of hydrogen passed for two days. The product is distilled in a current of steam, when, after the bulk of the methyl alcohol has been removed, a solid acid passes over with the condensed water. This, when collected and recrystallised from a very little formic acid, is obtained in glistening plates, melting at 71—73°. (Found, C = 69·1; H = 10·3. Calc., C = 69·2; H = 10·2 per cent.)

That this acid is 1-methyl*cyclo*hexyl-4-acetic acid was proved by mixing it with a specimen of the latter which we had previously obtained synthetically (Trans., 1908, **93**, 1081); the mixture melted at 71—73°. The reduction of 1-methyl*cyclo*hexylidene-4-acetic acid under the conditions described proceeds remarkably smoothly and is quite complete; this is shown by the fact that the acid obtained direct from the distillation in steam is stable towards permanganate.

On repeating this preparation with *d*- and *l*-1-methyl*cyclo*hexylidene-4-acetic acids, an optically inactive acid, identical with the above saturated acid, is in each case obtained. As was to be anticipated, the conversion of the optically active centroasymmetric acids into a product of which the molecule exhibits none of the characteristics of enantiomorphous configuration, results in the loss of the optical activity.

*4-Bromo-1-methyl*cyclo*hexyl-4-acetic Acid*,

$$CHMe{<}{}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}CBr\cdot CH_2\cdot CO_2H.$$

A reaction which resembles the above reduction in that it should convert the centroasymmetric optically active acid into a saturated substance which is potentially optically inactive, is involved in the addition of hydrogen bromide to the 1-methyl*cyclo*hexylidene-4-acetic acids. When the unsaturated *dl*-acid is mixed with fuming hydrobromic acid (saturated at 0°) it dissolves, but in a short time an oil, which rapidly crystallises, separates on the surface. The crystalline mass is washed with water, left in contact with porous earthenware until quite dry, and then recrystallised from a little formic acid (D = 1·22), in which it is very soluble, and from which it separates, usually in plates, but sometimes in hard, brilliant prisms. (Found, Br = 34·0. Calc., Br = 34·4 per cent.)

4-Bromo-1-methyl*cyclo*hexyl-4-acetic acid melts at 87°, and crystallises from light petroleum, in which it is readily soluble, in well-defined, glistening prisms with truncated ends; it is very readily soluble in methyl alcohol, ether, or benzene.

Similar experiments were made on the action of hydrobromic acid on *d*- and *l*-1-methyl*cyclo*hexylidene-4-acetic acids, and resulted in both cases in the production of an optically inactive bromo-acid identical in all respects with that obtained from the externally compensated unsaturated acid.

We have previously prepared this substance by the action of fuming hydrobromic acid on 4-hydroxymethyl*cyclo*hexyl-4-acetic acid (Trans., 1908, **93**, 1082); Wallach (*Annalen*, 1907, **353**, 312) made the same substance by treating the 1-methyl*cyclo*hexylidene-Δ^3-acetic acid of Marckwald and Meth with hydrobromic acid.

4-*Methylene*-1-*methyl*cyclo*hexane*,

$$\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\Big>\mathrm{C{:}CH_2}.$$

Finely divided 4-bromo-1-methyl*cyclo*hexyl-4-acetic acid dissolves readily in sodium carbonate solution, but the liquid gradually clouds, and an oil separates; the change occurs rapidly when the solution is warmed at 40°. The oil is extracted with ether, the ethereal extract carefully dried and evaporated, and the residue distilled; the whole quantity passes over at 122°, and the following results were obtained on analysis. (Found, C = 87·1; H = 12·8. Calc., C = 87·3; H = 12·7 per cent.)

Density at 19°/19° = 0·7923. Refractive index: $n_D = 1{\cdot}4465$ at 18°.

The molecular refraction: $M_D = 37{\cdot}06$; calculated, $M_D = 36{\cdot}43$.

There can be no doubt that this hydrocarbon is 4-methylene-1-methyl*cyclo*hexane, and identical with the compound which Wallach obtained (*Annalen*, 1906, **347**, 345; 1909, **365**, 267) by the slow distillation both of 1-methyl*cyclo*hexylidene-4-acetic acid and of 1-methyl-Δ^3-*cyclo*hexene-4-acetic acid, intramolecular change taking place in the latter case:

$$\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\Big>\mathrm{CBr\cdot CH_2\cdot CO_2H}\ \searrow$$

$$\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\Big>\mathrm{C{:}CH\cdot CO_2H} \longrightarrow \mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\Big>\mathrm{C{:}CH_2}.$$

$$\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2-CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\Big>\mathrm{C\cdot CH_2\cdot CO_2H}\ \nearrow$$

The hydrocarbon obtained by Wallach exhibited properties which are practically identical with those obtained by us, namely, boiling point, 122°; density at 20°/20° = 0·7920; $n_D = 1{\cdot}4450$ at 20°;

molecular refraction, $M_D = 36 \cdot 96$. The decomposition of 4-bromo-1-methyl*cyclo*hexyl-4-acetic acid by means of sodium carbonate solution appears to furnish an almost quantitative yield of pure 4-methylene-1-methyl*cyclo*hexane, and is therefore doubtless the best method at present available for the preparation of this interesting hydrocarbon.

Conversion of l-1-*Methyl*cyclo*hexylidene*-4-*acetic Acid into* dl-1-*Methyl*-Δ^3-cyclo*hexene*-4-*acetic Acid.*

It has been already shown (Trans., 1909, **95**, 1802) that 1-methyl*cyclo*hexylidene-4-acetic acid can be converted into the 1-methyl-Δ^3-*cyclo*hexene-4-acetic acid of Marckwald and Meth (*Ber.*, 1906, **39**, 1171 and 2404). In this reaction:

$$CHMe{<}{\genfrac{}{}{0pt}{}{CH_2 \cdot CH_2}{CH_2 \cdot CH_2}}{>}C{:}CH \cdot CO_2H \quad \text{to}$$

$$CHMe{<}{\genfrac{}{}{0pt}{}{CH_2{-}CH}{CH_2 \cdot CH_2}}{\geq}C \cdot CH_2 \cdot CO_2H,$$

a centroasymmetric substance is converted by intramolecular change into one containing an asymmetric carbon atom. Having previously studied this interconversion with the aid of the externally compensated 1-methyl*cyclo*hexylidene-4-acetic acid, we proceeded to examine the reaction which occurs when one of the optically active components of the above acid is converted. *l*-1-Methyl*cyclo*hexylidene-4-acetic acid (3 grams) is heated with sulphuric acid (24 grams), water (6 grams), and alcohol (30 c.c.) on the water-bath for three hours. After adding water and extracting with ether, the ethereal solution is washed with dilute sodium carbonate solution, which removes a small quantity of an acid, dried, and evaporated, the residue being left in a vacuum desiccator over sulphuric acid for some hours. The ester thus obtained was found to be optically inactive, and, on hydrolysis, yielded a syrupy acid, which soon crystallised; the oily impurity was removed by contact with porous earthenware, and a satiny, crystalline mass remained, which melted at 37—40° (compare Marckwald and Meth, *Ber.*, 1906, **39**, 1174). This consisted of 1-methyl-Δ^3-*cyclo*hexene-4-acetic acid, and was found to be optically inactive.

It is thus proved that the optically active 1-methyl*cyclo*hexylidene-4-acetic acid undergoes optical inversion during conversion into the isomeride which contains an asymmetric carbon atom. The formation of the latter externally compensated acid probably takes place in accordance with the following scheme. The elements of water are first taken up at the double linking in the optically active 1-methyl*cyclo*hexylidene-4-acetic acid (I), yielding the saturated 4-hydroxy-acid (II), of which the molecular configuration is not

enantiomorphous; this substance then loses water, with the formation of the externally compensated 1-methyl-Δ^3-*cyclo*hexene-4-acetic acid (III):

$$\mathrm{CHMe}{<}{}^{\mathrm{CH_2 \cdot CH_2}}_{\mathrm{CH_2 \cdot CH_2}}{>}\mathrm{C{:}CH \cdot CO_2H} \longrightarrow$$

(I.) Optically active.

$$\mathrm{CHMe}{<}{}^{\mathrm{CH_2 \cdot CH_2}}_{\mathrm{CH_2 \cdot CH_2}}{>}\mathrm{C(OH) \cdot CH_2 \cdot CO_2H} \longrightarrow$$

(II). Potentially inactive.

$$\mathrm{CHMe}{<}{}^{\mathrm{CH_2 - CH}}_{\mathrm{CH_2 \cdot CH_2}}{>}\mathrm{C \cdot CH_2 \cdot CO_2H.}$$

(III.) Externally compensated.

Addition of Bromine to 1-*Methyl*cyclo*hexylidene*-4-*acetic Acid.*

A reaction of more profound interest than those studied above is provided in the addition of bromine to 1-methyl*cyclo*hexylidene-4-acetic acid; the change involved is expressed by the transition:

$$\mathrm{{}^{CH_3}_{H}{>}C{<}{}^{\mathrm{CH_2 \cdot CH_2}}_{\mathrm{CH_2 \cdot CH_2}}{>}C{:}CH \cdot CO_2H} \quad \text{to}$$

$$\mathrm{{}^{CH_3}_{H}{>}C{<}{}^{\mathrm{CH_2 \cdot CH_2}}_{\mathrm{CH_2 \cdot CH_2}}{>}CBr \cdot CHBr \cdot CO_2H.}$$

For if, considering the carbon atoms (1) to (8) as lying in the same plane as the hydrogen atom (c), and the carbon and hydrogen atoms (9) and (a), as numbered on p. 1511, as lying in a plane approximately perpendicular to the foregoing (compare Trans., 1909, **95**, 1792), the modes in which the molecular configuration can take up bromine are traced, it will be seen that the two configurations of 1-methyl*cyclo*hexylidene-4-acetic acid can give rise to four stereoisomeric dibromides. In order clearly to understand the mode of production of two stereoisomeric dibromides from each of the optically active 1-methyl*cyclo*hexylidene-4-acetic acids, it is convenient to examine models of the various molecular configurations involved; these are depicted in the accompanying plate. When the unsaturated optically active 1-methyl*cyclo*hexylidene-4-acetic acid, of which the molecular configuration is depicted in Fig. 1, becomes saturated by the addition of bromine, two products may result. For if, in the diagrammatic formula on p. 1511 the (b) and (a) methyl radicle and hydrogen atom are supposed to lie respectively above and below the plane of the paper containing the centres of the carbon atom present in the hexamethylene ring, the two bonds of the ethylenic linking (4 : 7) must also lie above and below that plane. Either of these two components of the double bond may disappear owing to the substance becoming saturated by the addition of bromine, and, according as the lower

Fig. 1. Fig. 4.

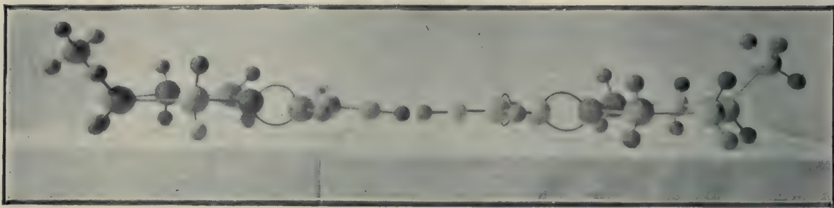


Fig. 2. Fig. 5.

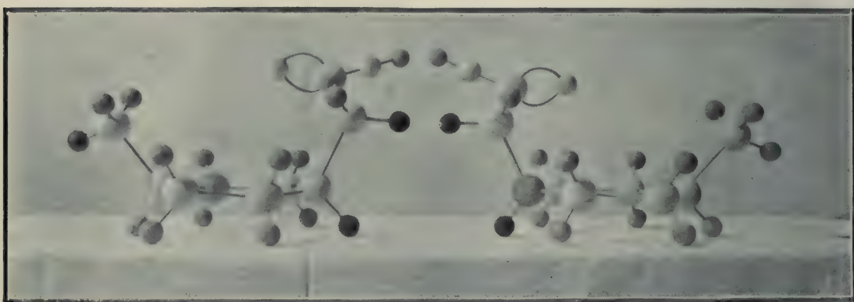
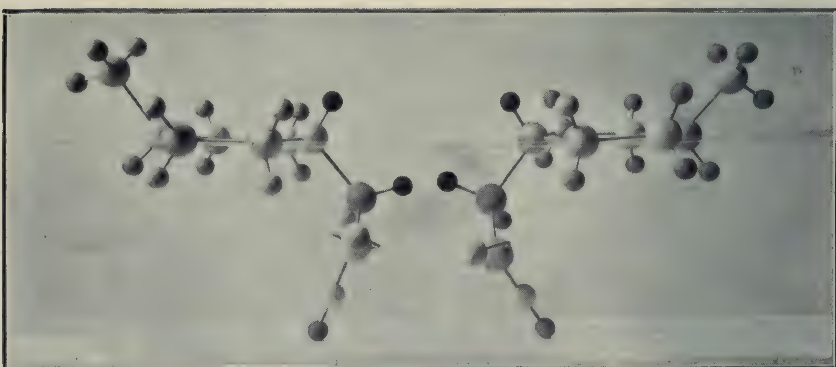


Fig. 3. Fig. 6.



[*To face* p. 1517.

or the upper bond is regarded as dissolved, the carbon atom (7) will, in the dibromide, bend towards the methyl group or towards the hydrogen atom (*a*) The configuration (Fig. 1) of the unsaturated acid will thus lead to the production of two dibromides, which differ in configuration as indicated in Figs. 2 and 3; similarly, the unsaturated acid (Fig. 4) enantiomorphously related to that shown in Fig. 1 will give rise to two dibromides (Figs. 5 and 6), of which the molecular configurations are enantiomorphously related respectively to those depicted in Figs. 2 and 3. The small spheres representing bromine atoms in Figs. 2, 3, 5, and 6 are painted black.

The original 1-methyl*cyclo*hexylidene-4-acetic acid only possesses one element of molecular asymmetry, and the dibromide produced therefrom only contains one asymmetric carbon atom in the molecule; the two enantiomorphously related modifications of the unsaturated acid should yield, however, four optically active isomerides of the saturated dibromide. For purposes of classification, therefore, it is convenient to regard the dibromides as exhibiting two elements of asymmetry, namely, a centroasymmetry exhibited by the right-hand part of the configurations of Figs. 1, 2, and 3, and an asymmetry of the carbon atom (7), as is shown in Figs. 2 and 3. It is thus evident that another new type of optically active substance may be realised, a type which combines the elements of centroasymmetry discussed above, as one asymmetric centre, with an asymmetric carbon atom, as a second asymmetric centre.

In view of the complexity of isomerism of the dibromides as indicated by the above discussion of the theoretical possibilities, it becomes of importance to investigate carefully the action of bromine on both the externally compensated and the optically active 1-methyl*cyclo*hexylidene-4-acetic acids in order to ascertain with certainty how many isomerides are actually produced during the addition of bromine. As the result of this study it has been found that the externally compensated and the optically active isomerides each yield two stereoisomeric dibromides. This accords entirely with the theoretical anticipations; as, however, we have at present no method for discriminating between configurations (2) and (3), it is convenient to distinguish the two stereoisomeric dibromides merely as the α- and β-isomerides in the present paper.

*α- and β-4-Dibromo-*dl-1-*methyl*cyclo*hexyl-4-acetic Acids.*

The action of bromine on *dl*-1-methyl*cyclo*hexylidene-4-acetic acid was studied in a variety of different ways, and the best results were obtained when the following conditions were observed.

The solution of the acid in a little dry chloroform is cooled to −10°, and gradually mixed with one molecular proportion of bromine dissolved in two volumes of chloroform; addition takes place readily. On exposing the product on a clock-glass to a current of air with frequent stirring, the syrupy residue soon commences to crystallise, and, after remaining for several days in the ice-chest, the mass, which still retains a considerable amount of oil, is left in contact with porous earthenware until quite dry. The colourless residue, consisting of a mixture of the α- and β-dibromides, is then digested with a large amount of light petroleum (b. p. 40—50°), which dissolves most of the α-isomeride and any oily impurity, and the residue, after several crystallisations from light petroleum (b. p. 70—80°), yields β-4-dibromo-*dl*-1-methyl*cyclo*hexyl-4-acetic acid as a hard, crystalline crust:

0·1471 gave 0·1863 CO_2 and 0·0610 H_2O. C = 34·5; H = 4·6.
0·2577 „ 0·3076 AgBr. Br = 50·8.
$C_9H_{14}O_2Br_2$ requires C = 34·4; H = 4·5; Br = 50·9 per cent.

β-4-*Dibromo*-dl-1-*methyl*cyclo*hexyl-4-acetic acid* melts at 145—146°, and is readily soluble in ethyl acetate, methyl alcohol, or warm benzene, but very sparingly so in light petroleum. It separates from benzene in well defined, elongated prisms, and from light petroleum in crusts consisting of groups of colourless needles.

For the purpose of separating the α-isomeride, the light petroleum mother liquors separated from the β-compound are allowed to evaporate, the semi-solid residue left in the ice-chest for several days, and then placed in contact with porous earthenware. After absorption of the oily impurity, the residue is crystallised several times from light petroleum; in this way the α-isomeride can be separated, although possibly not quite completely, from the β-compound described above:

0·1427 gave 0·1794 CO_2 and 0·0581 H_2O. C = 34·3; H = 4·5.
0·3014 „ 0·3584 AgBr. Br = 50·6.
$C_9H_{14}O_2Br_2$ requires C = 34·4; H = 4·5; Br = 50·9 per cent.

α-dl-1-*Methyl-4-dibromo*cyclo*hexyl-4-acetic acid* melts at about 106°, and separates, when its solution in light petroleum is allowed to evaporate spontaneously, as a crust composed of characteristic nodular masses of colourless needles. It is readily soluble in alcohol, ethyl acetate, chloroform, or benzene, but rather sparingly so in light petroleum (b. p. 40—50°).

A long series of experiments on the addition of bromine to *dl*-1-methyl*cyclo*hexylidene-4-acetic acid showed that the above two isomerides were apparently the only products formed during the reaction; these α- and β-isomerides are doubtless represented by the

molecular configurations depicted in Figs. 2 and 3. As is shown below, each is an externally compensated compound, so that the one represents the enantiomorphously related configurations 2 and 5, and the other the similarly related configurations 3 and 6.

d- *and* l-α- *and* β-*Dibromo*-1-*methyl*cyclo*hexyl*-4-*acetic Acids*,

$$CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CBr\cdot CHBr\cdot CO_2H.$$

The addition of bromine to the *d*- and *l*-1-methyl*cyclo*hexylidene-4-acetic acids, and the subsequent isolation of the products, is carried out in the same manner as that adopted in the treatment of the externally compensated acid. Using pure *d*- and *l*-acid having the specific rotatory power $[\alpha]_D + \text{and} - 81 \cdot 1°$, two optically active isomeric dibromides are obtained from each optically active acid; the optically active dibromides thus produced are the components of the externally compensated α- and β-dibromides described above. On repeatedly crystallising the bromination products of the optically active acids from light petroleum, the β-isomeride is obtained as a substance sparingly soluble in light petroleum, and crystallising therefrom in hard crusts composed of small, glistening prisms; it melts at 154°, and on crystallising together equal quantities of the β-isomerides produced from the enantiomorphously related acids, the externally compensated β-dibromide melting at 145—146° results. The optically active β-dibromo-1-methyl*cyclo*hexyl-4-acetic acids separate on slow evaporation of their solutions in ethyl acetate in lustrous, transparent crystals; Mr. A. Hutchinson, M.A., has kindly provided the following report, based upon measurements made by Mr. A. F. Hallimond on crystals of the *d*-β-isomeride.

"Crystal System: Tetragonal. $a:c = 1:1 \cdot 452$.

Forms observed: $m\{110\}$ and $p\{111\}$.

The crystals are of prismatic habit, terminated at each end by the pyramid faces, *p*, and are 4—5 mm. long and 1—2 mm. thick; only two crystals were available for measurement, and the prism faces were too rounded for reliable measurements to be obtained from them. Each crystal, however, afforded a good value for the angle between the two pyramid planes (111) and ($\bar{1}\bar{1}1$). The most reliable of these values was 128°4′, and from this the axial ratio quoted above was calculated. One of the crystals immersed in a liquid of refractive index 1·6, and viewed along the optic axial direction in convergent polarised light, exhibited a perfect uniaxial interference figure; no indication of circular polarisation was observed, nor could any evidence of the existence of a uniterminal

axis be obtained. In default of any evidence to the contrary, these crystals may therefore be provisionally assigned to the holohedral class of the tetragonal system. No cleavage was observed, the crystals breaking with a conchoidal fracture. The specific gravity, determined by the suspension method in Thoulet's solution, was found to be 1·827 at 21°, compared with water at 4°. The inclination of the pyramid planes was such as to permit the determination of both indices of refraction by the method of minimum deviation. The values obtained from the first crystal ($pp = 128°4'$) for sodium light were $\mu_o = 1·612$ and $\mu_e = 1·584$; the second crystal ($pp = 127°46'$) gave very similar values, namely, $\mu_o = 1·611$ and $\mu_e = 1·586$."

Although no evidence of enantiomorphous crystal structure was obtained, it can hardly be doubted that these crystals belong to one of the enantiomorphous classes of the tetragonal system (compare Pope, Trans., 1896, **69**, 971; Pope and Harvey, Trans., 1901, **79**, 828).

The following determinations of rotatory power were made:

β-Dibromo-1-methyl*cyclo*hexyl-4-acetic acid from

l-1-Methyl*cyclo*hexylidene-4-acetic acid. — *d*-1-Methyl*cyclo*hexylidene-4-acetic acid.

In benzene solutions.

l-series: 0·2983 gram in 20·05 c.c. at 16° in a 2-dcm. tube.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α ...	−0·87°	−0·75°	−0·73°
[α]...	−29·2	−25·2	−24·5

Dispersion: $Hg_{green}/Na_{yellow} = 1·192$. $Hg_{yellow}/Na_{yellow} = 1·029$

d-series: 0·4545 gram in 30 c.c. at 17° in a 4-dcm. tube.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α ...	+1·76°	+1·52°	+1·47°
[α]...	+29·0	+25·1	+24·3

Dispersion: $Hg_{green}/Na_{yellow} = 1·193$. $Hg_{yellow}/Na_{yellow} = 1·033$.

l-series: 0·6011 gram in 20·05 c.c. at 16° in a 2-dcm. tube.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α ...	−1·69°	−1·48°	−1·43°
[α]...	−28·2	−24·7	−23·9

Dispersion: $Hg_{green}/Na_{yellow} = 1·180$. $Hg_{yellow}/Na_{yellow} = 1·034$.

d-series: 0·9015 gram in 30 c.c. at 17° in a 4-dcm. tube.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α ...	+3·39°	+2·94°	+2·86°
[α]...	+28·2	+24·5	+23·8

Dispersion: $Hg_{green}/Na_{yellow} = 1·185$. $Hg_{yellow}/Na_{yellow} = 1·029$.

It is very difficult to obtain the β-dibromides in a state of high purity, and on recrystallising the *d*-isomeride several times from benzene the following values, slightly higher than the foregoing, were obtained for the rotatory powers:

0·4996 gram, made up to 30 c.c. with benzene, gave the values +1·96°, +1·71°, and +1·65° for the angle α with mercury green, mercury yellow, and sodium yellow light respectively in 4-dcm. tubes at 17°; the respective specific rotatory powers, [α], are thus +29·6°, +25·6°, and +24·3°, and the rotatory dispersions are, for $Hg_{green}/Na_{yellow} = 1·218$, and $Hg_{yellow}/Na_{yellow} = 1·053$.

Whilst the specific rotatory powers of this substance in benzene solution are moderately large and of the normal character, the

value for Hg_{green} being greater than that for Hg_{yellow}, and the latter, in turn, greater than that for Na_{yellow}, it is interesting to notice that the compound gives much lower values in ethyl acetate solution, and that in this solvent the dispersions are abnormal. The following determinations show that the specific rotatory powers for Hg_{green} and for the *D*-line are practically identical, whilst the value for Hg_{yellow} is appreciably smaller.

l-β-Dibromo-1-methyl*cyclo*hexyl-4-acetic acid. — *d*-β-Dibromo-1-methyl*cyclo*hexyl-4-acetic acid.

In ethyl acetate solutions.

1·0951 gram in 30 c.c. at 16°. — 0·5306 gram in 30 c.c. at 16°.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.		Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α ...	−0·34°	−0·27°	−0·34°	α ...	+0·16°	+0·14°	+0·17°
[α]...	−2·3	−1·9	−2·3	[α]...	+2·3	+2·0	+2·4

The optically active α-dibromo-1-methyl*cyclo*hexyl-4-acetic acids are much more readily soluble in light petroleum than are their β-isomerides; in view of the small quantities of material at our disposal and the difficulties encountered in the purification, we have only prepared the α-dibromide of *l*-1-methyl*cyclo*hexylidene-4-acetic acid in sufficient quantity for determination of the rotatory powers. The *d*- and *l*-isomerides separate from light petroleum in hard nodules, composed of colourless needles, which melt at 102°; their specific rotatory powers are opposite in sign to those of the parent acids.

1-α-Dibromo-1-methyl*cyclo*hexyl-4-acetic acid.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}/Na_{yellow}.	Hg_{yellow}/Na_{yellow}.
0·3015 gram, made up to 20·05 c.c. with benzene at 16°, in a 2-dcm. tube.					
α ...	+0·31°	+0·28°	+0·26°	1·20	1·08
[α]...	+10·3	+9·3	+8·6		
0·6104 gram, made up to 20·05 c.c. with benzene at 16°, in a 2-dcm. tube.					
α ...	+0·58°	+0·51°	+0·46°	1·25	1·10
[α]...	+9·5	+8·4	+7·6		
0·9986 gram, made up to 30 c.c. with ethyl acetate at 16°, in a 4-dcm. tube.					
α ...	+0·66°	+0·57°	+0·46°	1·25	1·10
[α]...	+4·9	+4·3	+3·9		

It is very remarkable that although the α-isomeride resembles the β-compound in giving much smaller specific rotatory powers in ethyl acetate than in benzene solution, the former shows about the same rotatory dispersion in the two solvents, whilst the latter exhibits quite abnormal dispersion in ethyl acetate solution. On crystallising together equal quantities of the *d*- and *l*-α-isomerides, the product is found to melt at 105—106°, the melting point of the externally compensated substance.

The fact, which we have now demonstrated, that, in accordance with the indications of theory, the two original centroasymmetric substances yield four optically active dibromides each of which is

a pure optically active compound, shows that the centroasymmetric structure is possessed of great configurational stability, and can be caused to undergo change in a perfectly definite manner without the occurrence of any optical inversion. It is possible, however, further to extend the work which leads to this conclusion, and to pass from the optically active dibromides, the optical activity of which is associated partly with centroasymmetry and partly with the presence of an asymmetric carbon atom, back again to substances of the purely centroasymmetric type.

Two changes of this kind are at once seen to be possible. On warming the dibromo-1-methyl*cyclo*hexyl-4-acetic acids with sodium carbonate solution, they should lose hydrogen bromide and carbon dioxide, giving 1-methyl-4-bromomethylene*cyclo*hexane in accordance with (1), whilst on heating with concentrated potash they should lose hydrogen bromide and yield 1-methyl*cyclo*hexylidene-4-bromoacetic acid in accordance with (2):

$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CBr\cdot CHBr\cdot CO_2H} \nearrow \quad \mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C{:}C}{<}\begin{matrix}\mathrm{H}\\ \mathrm{Br}\end{matrix} \quad \text{(I.)}$$

$$\searrow \quad \mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C{:}C}{<}\begin{matrix}\mathrm{CO_2H}\\ \mathrm{Br}\end{matrix} \quad \text{(II.)}$$

Both these reactions can be caused to proceed quantitatively, and both, when carried out with the pure optically active α- or β-dibromides, yield pure optically active centroasymmetric products.

*Externally Compensated 1-Methyl-4-bromomethylene*cyclo*hexane*,

$$\begin{matrix}\mathrm{H}\\ \mathrm{CH_3}\end{matrix}{>}\mathrm{C}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C{:}C}{<}\begin{matrix}\mathrm{Br}\\ \mathrm{H}\end{matrix}.$$

When the solution of the externally compensated modification of either α- or β-4-dibromo-1-methyl*cyclo*hexane-4-acetic acid in sodium carbonate solution is slightly warmed, it rapidly clouds, and the required bromo-hydrocarbon separates as a heavy oil. For the preparation of the substance in quantity, it is convenient to warm the crude product of the bromination of *dl*-1-methyl*cyclo*hexylidene-4-acetic acid with excess of sodium carbonate solution, and to distil the whole in a current of steam. The bromo-hydrocarbon, which is readily volatile with steam, is extracted with ether, the extract dried, evaporated, and the residue submitted to fractional distillation:

0·2165 gave 0·2179 AgBr. Br = 42·7.

$C_8H_{13}Br$ requires Br = 42·4 per cent.

dl-1-*Methyl*-4-*bromomethylene*cyclo*hexane* distils at 112—113° under 50 mm. or at 128° under 100 mm. pressure, and, when rapidly heated in small quantities under ordinary pressure, distils at 192° without profound decomposition. It has a pungent odour somewhat resembling that of *iso*amyl bromide; its stability is shown by the fact that it is only very slowly decomposed by boiling with sodium ethoxide in alcoholic solution. The chloroform solution of the compound readily absorbs one molecular proportion of bromine at −10°; some hydrogen bromide is, however, eliminated, and, after evaporation of the chloroform, the residual oil could not be caused to crystallise.

4-*Bromo*-4-*bromomethyl*-1-*methyl*cyclo*hexane*,

$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CBr\cdot CH_2Br}.$$

On shaking *dl*-1-methyl-4-bromomethylene*cyclo*hexane with fuming hydrobromic acid, saturated at 0°, it becomes converted into a very heavy oil. On distillation under reduced pressure most of the substance passes over at 120—125°/25 mm., but the appended analysis indicates that some decomposition with evolution of hydrogen bromide takes place under these conditions:

0·1571 gave 0·2092 AgBr. Br = 56·6.

$C_8H_{14}Br_2$ requires Br = 59·2 per cent.

d- *and* l-1-*Methyl*-4-*bromomethylene*cyclo*hexane*,

$$\begin{matrix}\mathrm{CH_3}\\ \mathrm{H}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C{:}C}<\begin{matrix}\mathrm{Br}\\ \mathrm{H}\end{matrix}.$$

The *α*- and *β*-isomerides, either of *d*- or *l*-1-methyl*cyclo*hexylidene-4-acetic acid, yield the same product on treatment with sodium carbonate solution under the conditions specified above; the resulting bromo-hydrocarbon is a heavy oil with a pungent odour, which boils at 112—113°/50 mm.

The following determinations of rotatory power were made:

d-1-Methyl-4-bromomethylene*cyclo*hexane dissolved in light petroleum at 16° in 4-dcm. tubes.

3·0051 grams in 30 c.c.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α......	−23·79°	−20·97°	−20·19°
[α] ...	−59·37	−52·34	−50·39

l-1-Methyl-4-bromomethylene*cyclo*hexane dissolved in light petroleum at 16° in 4-dcm. tubes.

3·0579 grams in 30 c.c.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α.....	+24·10°	+21·27°	+20·43°
[α] ...	+59·11	+52·17	+50·18

Mean dispersions: Hg_{green}/Na_{yellow} = 1·178. Hg_{yellow}/Na_{yellow} = 1·040.

In absolute alcoholic solution

1·0158 grams in 30 c.c. at 16° in a 4-dcm. tube.

				Hg_{green}/Na_{yellow}.	Hg_{yellow}/Na_{yellow}.
α......	−8·43°	−7·50°	−7·21°		
[α] ...	−62·24	−55·38	−50·4	1·179	1·041.
[M]...	−117·6	−104·7	−100·6		

It will be seen that during the series of reactions by means of which the replacement of a hydrogen atom by bromine and of the carboxyl group by a hydrogen atom has been effected in the original 1-methyl*cyclo*hexylidene-4-acetic acid, the sign of the optical activity has been reversed; at no stage during the series, however, has any indication of optical inversion been obtained. The rotatory dispersions are practically the same, whether light petroleum or ethyl alcohol is used as the solvent.

d- *and* l-1-*Methyl*cyclo*hexylidene*-4-*bromoacetic Acid*,

$$\frac{CH_3}{H}\!>\!C\!<\!\frac{CH_2\cdot CH_2}{CH_2\cdot CH_2}\!>\!C\!:\!C\!<\!\frac{CO_2H}{Br}.$$

Pure *l*-α-4-dibromo-1-methyl*cyclo*hexyl-4-acetic acid (m. p. 154°, $[\alpha]_D$ −24·5°) was stirred into a paste with very little water, mixed with ten parts of 50 per cent. potassium hydroxide solution, and rapidly heated to boiling over a naked flame; in a few seconds the liquid clouded, and, on cooling, a potassium salt separated in quantity. The alkaline liquid was decanted as completely as possible, the salt washed with a little 50 per cent. potassium hydroxide solution, dissolved in water, acidified with hydrochloric acid, and the syrupy acid extracted with ether. After drying and evaporating, a nearly colourless syrup remained, which, when left for some days in the ice-chest and persistently rubbed, ultimately solidified. The crystals were squeezed between two pieces of porous earthenware, and then became perfectly colourless; the material was, however, so readily soluble in organic solvents that it was found impossible to recrystallise the small quantity which we had at our disposal. For the purpose of further purification it was therefore dissolved in light petroleum (b. p. 40—50°), the filtered solution evaporated, and the mass, as soon as crystallisation was nearly complete, rapidly transferred to porous porcelain; this operation was twice repeated, and the substance then analysed:

0·1511 gave 0·1201 AgBr. Br = 33·8.

$C_9H_{13}O_2Br$ requires Br = 34·3 per cent.

l-1-*Methyl*cyclo*hexylidene*-4-*bromoacetic acid* melts approximately at 50°; the identity of our product was controlled by the following titration: 0·3128 gram of the acid, dissolved in dilute alcohol, required, for neutralisation, 13·5 c.c. of *N*/10-NaOH, whereas this quantity of the monobasic acid, $C_9H_{13}O_2Br$, should neutralise 13·4 c.c.

The following determinations of rotatory power were made with 1-methyl*cyclo*hexylidene-4-bromoacetic acid in alcoholic solutions, 4-dcm. tubes being used:

0·4906 gram in 30 c.c. at 19°.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	−0·81°	−0·72°	−0·68°
[α]......	−12·4	−11·0	−10·4
[M] ...	−28·9	−25·6	−24·2

0·8900 gram in 30 c.c. at 16°.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	−1·44°	−1·26°	−1·22°
[α]	−12·1	−10·6	−10·3
[M] ...	+28·2	−24·7	−24·0

Mean dispersions: $Hg_{green}/Na_{yellow} = 1·18$. $Hg_{yellow}/Na_{yellow} = 1·02$.

On repeating this preparation, using *d*-β-dibromo-1-methyl*cyclo*hexyl-4-acetic acid, a product was obtained which gave the specific rotatory power [α] for the Hg_{green} line of +12·8°. It is thus proved that the α- and β-dibromides derived from one optically active 1-methyl*cyclo*hexylidene-4-acetic acid yield the same optically active 1-methyl*cyclo*hexylidene-4-bromoacetic acid under the conditions prescribed above.

d-1-*Methyl*cyclo*hexylidene*-4-*acetic Acid*,

$$\begin{matrix}CH_3\\H\end{matrix}\!>C<\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!>C:C<\!\begin{matrix}CO_2H\\H\end{matrix}.$$

A curious numerical relation has been observed between the molecular rotatory powers of the centroasymmetric substances with which we are now concerned; this made it important to obtain more complete data than those given in our previous papers for the rotation constants of 1-methyl*cyclo*hexylidene-4-acetic acid. The following determinations were made with a highly purified specimen of the *d*-acid: 0·2608 gram was made up to 30 c.c. with absolute alcohol, and examined in a 4-dcm. tube at 18°:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}/Na_{yellow}.	Hg_{yellow}/Na_{yellow}.
α	+3·33°	+2·91°	+2·82°	1·181	1·032
[α]......	+95·8	+83·7°	+81·1		
[M] ...	+147·6	+129·0	+125·0		

The following table states the molecular rotatory powers in alcoholic solution of the centroasymmetric compounds described in the present paper.

Molecular Rotatory Powers.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
(1) $d\text{-R:C}<\begin{matrix}H\\H\end{matrix}$	0	0	0
(2) $d\text{-R:C}<\begin{matrix}H\\CO_2H\end{matrix}$	+147·6°	+129·0°	+125·0°
(3) $d\text{-R:C}<\begin{matrix}Br\\H\end{matrix}$	−117·6	−104·7	−100·6
Algebraic sums of (2) and (3):	+30·0	+24·3	+24·4
(4) $d\text{-R:C}<\begin{matrix}Br\\CO_2H\end{matrix}$	+28·9	+25·6	+24·0

On replacing the lower hydrogen atom in (1) by carboxyl, as in (2), the molecular rotatory power changes from zero to the positive value given under (2). On replacing the upper hydrogen atom in (1) by bromine, the molecular rotatory powers similarly change from zero to the negative values given under (3). On making both of the above substitutions simultaneously, the effect on the original rotatory power of zero of (1) is, within the limits of experimental error, found to be the algebraic sum of the two substitutions performed separately. The algebraic sums of the molecular rotatory powers of (2) and (3) are thus very nearly equal to the corresponding molecular rotatory powers of (4). The angular changes in molecular rotatory power brought about by these substitutions are roughly proportional to the atomic or molecular volumes of the substituting groups.

The Relation between Optical Activity and Asymmetry of Atomic Environment.

It has been frequently suggested that asymmetry of a carbon atom is not alone a sufficient indication of optical activity, but that a certain complexity of molecular constitution must necessarily accompany enantiomorphism of molecular configuration if stable optical activity is to result. This suggestion is, of course, based on the view that if the asymmetry of a particular atom depends on the attachment to that atom of three or four single and different atoms, isomeric change may well determine the optical inversion of any optically active individual component of the synthetic material. The only positive experimental evidence opposed to the above suggestion is apparently the observation of Swarts (*Bull. Acad. Roy. Belg.*, 1896, [iii], **31**, 28) to the effect that fluorochlorobromoacetic acid, $CFClBr{\cdot}CO_2H$, can be caused, by crystallisation with strychnine or cinchonine, to yield a component exhibiting fugitive optical activity. Much negative evidence in support of the suggestion mentioned is, however, available (Pope and Read, Trans., 1908, **93**, 794).

Obviously, the difficulty of obtaining a solution of the problem suggested above is largely due to the difficulty of synthesis of the materials required for the experimental work. These difficulties, however, are to a large extent removed by the discovery of the optically active centroasymmetric compounds. We are now able to prepare from optically active centroasymmetric substances compounds of which the optical activity is associated with the presence of a single asymmetric carbon, the asymmetry being determined by the attachment of one complex group and three single atoms to one particular carbon atom.

Thus, the optically active centroasymmetric 1-methyl-4-bromomethylene*cyclo*hexanes are, by treatment with chlorine, convertible into derivatives of the simple asymmetric character just premised:

$$\begin{matrix}CH_3\\ H\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}Br\\ H\end{matrix} \quad \text{to} \quad \begin{matrix}CH_3\\ H\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!>\!CCl\cdot C\!\begin{matrix}/Br\\ -Cl\\ \backslash H\end{matrix}.$$

Similarly, the optically active 1-methyl*cyclo*hexylidene-4-bromoacetic acids should take up chlorine to yield a dichloride which contains an asymmetric carbon atom attached to a bromine and a chlorine atom:

$$\begin{matrix}CH_3\\ H\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}CO_2H\\ Br\end{matrix} \quad \text{to}$$

$$\begin{matrix}CH_3\\ H\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!>\!CCl\cdot C\!\begin{matrix}/CO_2H\\ -Cl\\ \backslash Br\end{matrix}.$$

It must be noted that it is not to be anticipated that, starting from a pure optically active 1-methyl*cyclo*hexylidene-4-bromoacetic acid or 1-methyl-4-bromomethylene*cyclo*hexane, a single product should be obtained; the respective dichlorides furnish a case of isomerism identical in character with that of the *l*-dibromo-1-methyl*cyclo*hexyl-4-acetic acids, and should consequently be formed as mixtures of an α- and a β-isomeride, just as described in connexion with the latter acids.

l-4-*Chloro*-1-*methyl*cyclo*hexyl*-4-*chlorobromoacetic Acid*,

$$\begin{matrix}CH_3\\ H\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!>\!CCl\cdot C\!\begin{matrix}/CO_2H\\ -Cl\\ \backslash Br\end{matrix}.$$

Pure *l*-1-methyl*cyclo*hexylidene-4-bromoacetic acid is dissolved in three volumes of glacial acetic acid, the solution cooled to $-5°$, and a slow stream of chlorine passed until addition is complete and the liquid has acquired a yellow colour. During the whole operation the apparatus is enveloped in black paper, and, after remaining overnight in the ice-chest, the product is dissolved in ether, thoroughly washed with water, dried, and the ether evaporated at a low temperature. The almost colourless residue was left over phosphoric oxide and sulphuric acid in a vacuum desiccator for two days, and then analysed:

0·0963 gave 0·1453 AgCl,AgBr. $Cl_2Br = 49{\cdot}1$.

$C_9H_{13}O_2Cl_2Br$ requires $Cl_2Br = 49{\cdot}6$ per cent.

This dichlorobromo-acid is a viscid syrup, which on long preservation in the ice-chest becomes partially crystalline; it is feebly lævorotatory, as is indicated by the appended determinations.

0·9485 gram, made up to 25 c.c. with absolute alcohol, and examined in a 4-dcm. tube at 17°, gave the following values:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}/Na_{yellow}.	Hg_{yellow}/Na_{yellow}.
α......	−0·20°	−0·17°	−0·16°	1·26	1·07
$[\alpha]$...	−1·32	−1·12	−1·05		

The small values obtained for the specific rotatory powers of this substance, together with the fact that we have been unable to treat the compound by methods which would ensure its purity, might lead to three suggestions which would account for the slight optical activity observed. It may be suggested (1) that the optical activity is due to the presence of 1-methyl*cyclo*hexylidene-4-bromoacetic acid which had escaped addition of chlorine, or (2) that during the addition of the halogen considerable optical inversion had occurred. The suggestion (1) must, however, be abandoned because the rotatory dispersions of the dichloride, namely, 1·26 and 1·07, are appreciably different from those for the original unsaturated bromo-acid, namely, 1·18 and 1·02; it is thus impossible to attribute the optical activity to the presence of unaltered 1-methyl*cyclo*hexylidene-4-bromoacetic acid. With regard to suggestion (2) it should be remarked that no optical inversion was observed during the addition of bromine to the optically active 1-methyl*cyclo*hexylidene-4-acetic acids, and that the product, in the latter cases, consisted of a mixture of the α- and β-isomerides which exhibited specific rotatory powers of opposite signs. It is thus scarcely to be doubted (3) that the *l*-4-chloro-1-methyl*cyclo*hexyl-4-chlorobromo-acetic acid with which we are now dealing is a mixture of the α- and β-lævo-isomerides exhibiting rotatory powers of opposite signs; that two isomerides of the α- and β-type are present is, of course, strongly indicated by the fact that the substance slowly becomes partially crystalline.

d-4-*Chloro*-1-*methyl*-4-*chlorobromomethyl*cyclo*hexane*,

$$\begin{matrix}CH_3\\H\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!\!>\!CCl\cdot C\!\begin{matrix}\diagup Br\\ -Cl.\\ \diagdown H\end{matrix}$$

The *d*-1-methyl-4-bromomethylene*cyclo*hexane used in the preparation of the above compound was the lævorotatory modification obtained by the action of sodium carbonate on the dibromides of *d*-1-methyl*cyclo*hexylidene-4-acetic acid; the latter acid exhibited $[\alpha]_D$ +81·1°.

The solution of this bromo-hydrocarbon in acetic acid is cooled to −5°, carefully protected from light, and saturated with dry chlorine; after remaining for twenty-four hours in the ice-chest,

water is added, the heavy oil extracted with ether, the ethereal solution washed thoroughly with water and sodium carbonate solution, dried, and evaporated. An oil is thus obtained which distils almost completely at 171—173°/35 mm., only a small quantity of a residue of higher boiling point being left in the distilling flask; after redistillation the material was analysed:

0·1086 gave 0·2005 AgCl,AgBr. $Cl_2Br = 58·7$.

$C_8H_{13}Cl_2Br$ requires $Cl_2Br = 58·1$ per cent.

This dichlorobromo-hydrocarbon is a colourless oil, which does not appear to undergo any decomposition when distilled under diminished pressure; it has the pungent odour characteristic of substances of similar composition:

1·0710 gram, made up to 30 c.c. with absolute alcohol at 17°, and examined in a 4-dcm. tube, gave the following results:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}/Na_{yellow}.
α......	+0·055°	+0·05°	+0·05°	1·10
[α] ...	+0·39	+0·35	+0·35	

The discussion given above of the cause of the optical activity of the last compound described is immediately applicable to the present one; the optical activity cannot be attributed to the presence of unchlorinated substance, because the parent compound exhibits a specific rotatory power opposite in sign to that of the saturated halogen derivative of the hydrocarbon. In this, as in the preceding, case the low specific rotatory power is doubtless due to the preparation being a mixture of a dextro- and a lævo-rotatory α- and β-isomeride.

Our thanks are due to Dr. John Read for the care with which he has carried out much of the experimental work involved in the present paper.

The Chemical Department,
The University, Manchester.

The Chemical Laboratory,
The University, Cambridge.

CLXXIII.—*Some Reactions of Gum Kino.*

By John Lionel Simonsen.

During the course of a number of researches on Indian products which are in progress in these laboratories, the attention of the author was directed to the constituents of the gum kino obtained from *Pterocarpus Marsupium*.

Kino was first subjected to a careful investigation by Etti (*Ber.*, 1878, **11**, 1879), who stated that when kino was heated with dilute hydrochloric acid, in addition to a deep red phlobaphen, kino red, a crystalline substance could be extracted with ether. To this substance he gave the name kinoin, and the formula $C_{14}H_{12}O_6$. He, however, isolated only a very small quantity of this compound, and did not subject it to any careful examination beyond suggesting that it contained a methoxy-group and readily passed into kino red. The only other mention of this substance in the literature is a short note by A. G. Perkin and Yoshitake (Trans., 1902, **81**, 1173) at the conclusion of their investigations on catechin, in which they state that they isolated kinoin, and tested its tinctorial properties.

Considerable doubt as to the existence of this substance was caused by the work of E. White (*Pharm. J.*, 1903, [iv], **16**, 676), who stated that he was quite unable to obtain any kinoin from kino obtained from Malabar.

Since it seemed possible to the author that kinoin might be closely related to catechin, it was thought worth while to subject kino to thorough re-investigation. The kino which was used in this research was of undoubted authenticity, and it was obtained for the author by Dr. J. R. Henderson, Superintendent of the Madras Museum, to whom he wishes to express his thanks for his kind assistance.*

As a preliminary step, Etti's experiments (*loc. cit.*) were very carefully repeated, using the quantities and the conditions recommended by him. In no experiment was it found possible, however, to isolate any trace of kinoin. In some experiments a very small amount of a crystalline substance was obtained, which showed all the properties of catechol. The presence of catechol is readily explained by the fact that crude gum kino itself always contains a small quantity of this substance, which may be extracted from

* In investigating natural products, the age of the substances is a matter of considerable importance. In the author's preliminary experiments, kino of unknown age was used, but in the later experiments freshly collected and undried gum was employed. It may perhaps be mentioned that in this case no difference in the results obtained was noticed.

it with ether. Since hydrolysis with dilute hydrochloric acid did not result in the production of any kinoin, experiments were instituted with other hydrolytic agents. In no case, however, was any kinoin obtained.

Kino itself, when dried, is a deep red, brittle, amorphous solid. Its properties, especially with regard to its tanning power, have been very carefully studied by Hooper (*Indian Agric. Ledger*, 1901, No. 11). Since it was found impossible to purify this gum in any way, attention was directed to its derivatives. Kino is readily methylated when treated with methyl sulphate and potassium hydroxide.* The *methyl ether* thus obtained is an almost colourless, amorphous powder, which could not be crystallised. It was purified by precipitation from alcohol, and gave on analysis figures agreeing with the formula $C_{15}H_{11}O_4(OMe)_3$. In order to obtain some confirmation of these figures, the *acetate* was also prepared in the usual manner, and was isolated as an amorphous, brown powder. On analysis it gave figures closely agreeing with those required by the formula $C_{15}H_{11}O_4(OAc)_3$. At my request Mr. Ramaswami Krishna Iyer, M.A., kindly made a molecular-weight determination of kino methyl ether, since the general properties of these substances indicated that they must have a higher molecular weight than that required by the simple formula $C_{15}H_{11}O_4(OH)_3$ for kino. The results of this determination (see p. 1533) show clearly that kino methyl ether has a molecular weight at least twice that required by the simplest formula. Whether it is possible, however, to place much reliance on this result is doubtful, since it is probable that the ether exists in solution as a colloid. This determination is of some interest, since it has been shown recently by Iljin (*J. pr. Chem.*, 1910, [ii], **82**, 422) that the molecular weight of tannin must be much higher than is suggested by the work of Nierenstein.

When kino methyl ether is oxidised in the cold with potassium permanganate, the only product of the oxidation is veratric acid. It was stated by Hlasiwetz (*Annalen*, 1865, **134**, 122) that when kino was fused with potassium hydroxide, it yielded protocatechuic acid and phloroglucinol. The production of veratric acid supported this statement, but no trace of a phloroglucinol derivative could be isolated. The presence of such a nucleus in kino was further rendered doubtful by the fact that on repeating the fusion of kino with potassium hydroxide only protocatechuic acid and catechol could be isolated, there being no indication of any trace of phloroglucinol.

* The author can confirm the statement of White (*loc. cit.*) with reference to the absence of a methoxy-group in kino.

An interesting result was obtained when kino itself or the phlobaphen, kino red, was oxidised with dilute nitric acid. When the oxidation is carried out under the conditions described in the experimental part of this paper (p. 1534), the product consists of a mixture of oxalic acid and ammonium quadroxalate. The formation of this ammonium salt during the course of an oxidation in which excess of acid is present is extremely remarkable. The ammonia can obviously only be due to the reduction of some of the nitric acid, and its formation is a proof of the extraordinary reducing power of kino. Ammonium quadroxalate is a salt of very great stability, and is not readily decomposed by acids, since it may be crystallised from concentrated hydrochloric acid, and is not acted on by concentrated nitric acid at 100°. It seems doubtful if it can have the normal structure, and experiments are in progress with the view of elucidating this point.

Experimental.

Although numerous attempts were made to purify the crude gum, it was found quite impossible to obtain it in a crystalline form and free from inorganic contamination. It showed all the properties ascribed to it by Hooper (*loc. cit.*), and behaved in the usual manner with tannin reagents.

Kino Methyl Ether.

In carrying out the methylation of kino, the following method was found, after numerous trial experiments, to give the most satisfactory results. Kino (15 grams) was dissolved in alcohol, and methyl sulphate (19 grams) was added. To this mixture potassium hydroxide (9 grams) dissolved in water (10 c.c.) was added all at once. In a short time the mixture became very hot, and the reaction was controlled by cooling with cold water. After some time the same amounts of methyl sulphate and potassium hydroxide were added, and when all reaction had ceased, the solution was diluted, and the amorphous solid (15 grams) which separated, collected and well washed with water.

The crude kino methyl ether obtained in this manner was purified by repeated precipitation from alcohol with water, when it was found to be an almost colourless, amorphous powder, which could not be crystallised. It was quite free from ash, and two distinct preparations gave the following results on analysis, after drying at 110°:

0·1912 gave 0·437 CO_2 and 0·0999 H_2O. C = 62·3; H = 5·8.
0·1561 „ 0·3533 CO_2 „ 0·0767 H_2O. C = 61·7; H = 5·5.
0·1288 „ 0·2633 AgI. MeO = 26·9 per cent.
$C_{15}H_{11}O_4(OMe)_3$ requires C = 62·1; H = 5·7; MeO = 26·7 per cent.

Kino methyl ether does not melt at 300°, and is readily soluble in most organic solvents. It is insoluble in alkalis, and its alcoholic solution gives no colour with ferric chloride. It dissolves in concentrated sulphuric acid with a purple-red colour.

A determination of its molecular weight by the cryoscopic method, using naphthalene as a solvent, gave the following result:

0·374, in 25·4 naphthalene, gave Δt 0·126. M.W. = 818.
$(C_{18}H_{20}O_7)_2$ requires M.W. = 696.

The question as to the value which can be attached to this result has already been discussed (p. 1531).

Acetylkino.

In preparing this substance, kino (5 grams) was mixed with acetic anhydride (15 grams) and anhydrous sodium acetate (3 grams), and heated for about an hour on the sand-bath. During the heating the kino passes into solution, and, after cooling, the deep red reaction-mixture was poured into water, when the acetylkino separated out as a brown powder.

Acetylkino, which, like kino methyl ether, could not be obtained crystalline, was purified by repeated precipitation from acetic acid solution with water. By this means it was obtained as a pale brown powder, readily soluble in most solvents, and showing no characteristic colour reactions. For analysis it was dried at 110°, two distinct preparations being used. The acetyl group determination was made by A. G. Perkin's method:

0·1329 gave 0·2835 CO_2 and 0·0571 H_2O. C = 58·2; H = 4·8.
0·132 „ 0·2823 CO_2 „ 0·0578 H_2O. C = 58·3; H = 4·9.
0·1519 „ 0·0631 $C_2H_4O_2$. $C_2H_4O_2$ = 41·5.
$C_{15}H_{11}O_4(O{\cdot}CO{\cdot}CH_3)_3$ requires C = 58·3; H = 4·6;
$C_2H_4O_2$ = 41·7 per cent.

Action of Hydrochloric Acid on Kino.

In carrying out these experiments, Etti's method (*loc. cit.*) was used. Kino (50 grams) was mixed with dilute hydrochloric acid (100 grams), and heated to boiling on the sand-bath. The kino passes into solution, and in a short time the whole liquid is filled with a bright red, somewhat gelatinous mass consisting of kino red. After boiling

for half an hour, the hot solution was filtered, cooled, and after saturation with ammonium sulphate, the red solution was extracted with ether. On removing the ether, a small quantity of an oil was obtained, which crystallised, and was found to consist of catechol. No trace of kinoin could be obtained, although the experiment was repeated numerous times, using different conditions. Careful examination also proved the absence of any sugar, showing that kino is not glucosidic in character.

Fusion of Kino with Potassium Hydroxide.

Kino (5 grams) was gradually added to molten potassium hydroxide (50 grams) containing a little water. When all the kino had been added, the temperature was raised to 190—210°, and finally for a few minutes to 250°. After cooling, the deep brown fusion was dissolved in water, hydrochloric acid was added until the solution was just acid, and the solution extracted with ether, the ether well washed with sodium hydrogen carbonate to remove acids, dried, and evaporated, when an oil was obtained. This oil partly solidified, and the solid was drained on porous porcelain, and found to consist of catechol. Sufficient of the oily phenol could not be obtained for identification, but no trace of phloroglucinol was detected.

The sodium hydrogen carbonate solution containing the acid was acidified, and extracted with ether, when, on removing the ether, a solid was obtained, which, after crystallisation from water, melted at 197—198°, and was identified as protocatechuic acid.

Oxidation of Kino Methyl Ether.

In carrying out this oxidation, kino methyl ether (10 grams) was suspended in dilute sodium carbonate solution, and shaken in the cold with potassium permanganate until a permanent pink colour was obtained. After filtering from manganese dioxide, the solution, which had a strong odour of vanillin, was concentrated on the water-bath, acidified, and after being saturated with ammonium sulphate, extracted with ether. On removing the ether, a viscous oil remained, which rapidly solidified. After draining on porous porcelain, it was crystallised from hot water, when it melted at 178—179°, and showed all the properties of veratric acid. (Found, C=59·2; H=5·5. Calc., C=59·3; H=5·5 per cent.)

Oxidation of Kino and Kino Red with Nitric Acid.

It has already been mentioned (p. 1531) that when kino or kino red is oxidised with dilute nitric acid, the double salt of oxalic

acid, ammonium quadroxalate is formed. Since the conditions in both oxidations were the same, only the oxidation of kino red is described.

Kino red (5 grams) was mixed with nitric acid (10 per cent.) (30 c.c.), and allowed to remain in the cold with constant shaking. The mixture gradually becomes warm, and in order to prevent the reaction becoming too vigorous it is necessary to cool the flask in running water. After remaining in the cold for twelve hours, the reaction was completed by warming on the water-bath for five to six hours. The solution was filtered from some unattacked kino red, and the deep brown filtrate concentrated on the water-bath, when, on cooling, ammonium quadroxalate separated in large, hexagonal rhombohedra (yield 1 gram). The mother liquor on concentration gave a small quantity of oxalic acid.

Ammonium quadroxalate, which was purified by crystallisation from water, melts and decomposes at 130°, and crystallises with two molecules of water of crystallisation. (Found, C=20·5, 20·2; H=4·8, 4·7; N=6·3. Calc., C=20·6; H=4·7; N=6·0 per cent.) That this substance was ammonium quadroxalate was confirmed by direct comparison with a specimen prepared from oxalic acid and ammonium oxalate.

THE PRESIDENCY COLLEGE,
MADRAS.

CLXXIV.—*Synthesis of Derivatives of Thioxanthone. Part III.* 1 : 4-*Dihydroxythioxanthone.*

By HANS THACHER CLARKE and SAMUEL SMILES.

IN addition to the various general methods now available (Meyer, *Ber.*, 1909, **42**, 1134; Davis and Smiles, Trans., 1910, **97**, 1290; Marsden and Smiles, this vol., p. 1353; Smiles, Proc., 1910, **26**, 342) for the synthesis of derivatives of thioxanthone, another has been devised which is especially suitable for the production of dihydroxy-derivatives. The experiments described in the present paper have been carried out in illustration of this method, and the synthesis of 1:4-dihydroxythioxanthone is described.

The process may be accomplished in two stages, of which the first consists of the union of *o*-thiolbenzoic acid with a quinone. The interaction of quinones and aromatic mercaptans has been studied by Tröger and Eggert (*J. pr. Chem.*, 1896, [ii], **53**, 482), who found that an excess of phenyl mercaptan reacts with *p*-benzoquinone,

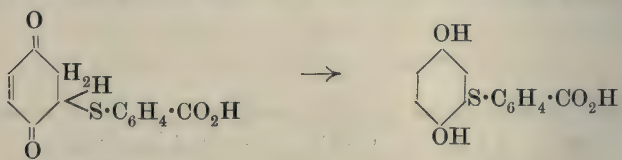
giving an additive product of the composition $C_6H_4O_2,2C_6H_5{\cdot}SH$. Posner (*Annalen*, 1904, **336**, 85), in re-investigating this substance, showed that addition of the mercaptan takes place at the ethylenic groups of the quinonoid nucleus (as in I); but since the substance appeared to behave in the hydroxylic form (II), he represented it by the following tautomeric scheme:

(I.) (II.)

More recently the interaction of equimolecular proportions of *p*-benzoquinone and sulphydric derivatives has been described in patent literature (Badische Anilin- und Soda-Fabrik, D.R.-P. 175070). Thus monothio-derivatives are obtained according to the equation:

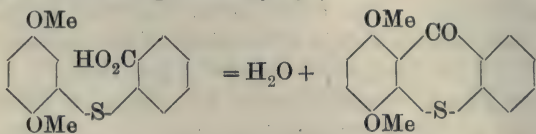
$$C_6H_4O_2 + RSH = C_6H_4(OH)_2{\cdot}SR,$$

where R represents an acid group, either organic or inorganic. We find that a similar interaction occurs between *o*-thiolbenzoic acid and quinones. According to the interpretation given by Posner to this type of reaction, it is evident that the product from that acid and *p*-benzoquinone would be the dihydro-derivative (III):



(III.) (IV.)

but since the substance obtained behaves according to the hydroxylic structure, we prefer to represent it as the derivative of quinol (IV), which is evidently produced from the dihydro-compound by intramolecular rearrangement. Thus, when the substance is methylated in alkaline solution, it yields a dimethyl derivative, which must be formulated as containing methoxyl (V):



(V.) (VI.)

for on treatment with cold sulphuric acid, this yields 1:4-dimethoxythioxanthone (VI), the latter being identical with the product

obtained from *o*-dithiobenzoic acid and the dimethyl ether of quinol:

$$C_6H_4<\begin{matrix}CO_2H\\ S\cdot OH\end{matrix} + C_6H_4(OMe)_2 = C_6H_4<\begin{matrix}CO\\ -S-\end{matrix}>C_6H_2(OMe)_2 + 2H_2O.$$

The parent substance—1:4-dihydroxythioxanthone (VI)—is readily obtained from the dihydroxy-sulphide (IV) by treatment with dehydrating agents. This compound is deep orange, and furnishes crimson salts with alkaline hydroxides; but it is of little value as a dyestuff, since it does not form lakes, and the alkali salts are very readily oxidised.

The synthetical method which is illustrated in this paper appears to be capable of wide, although not universal, application.

Experimental.

2′-*Carboxy*-2 : 5-*dihydroxydiphenyl Sulphide*, $C_6H_3(OH)_2\cdot S\cdot C_6H_4\cdot CO_2H$.

Five and a-half grams of *p*-benzoquinone were dissolved in about 150 c.c. of cold glacial acetic acid, and, while the mixture was constantly shaken, a thin paste made of 7·7 grams of *o*-thiolbenzoic acid with the same medium was added. After the lapse of twenty-four hours a small quantity of *o*-dithiobenzoic acid was removed by filtration from the red-coloured liquid; the latter was then evaporated on the water-bath with continual addition of water until the bulk of the acetic acid was expelled. When a suitable concentration was reached, sulphurous acid was added, and the liquid was filtered while hot. On cooling the solution a crystalline mass of the required acid was deposited. This was recrystallised from hot water, from which the substance separated in small, colourless prisms, melting at 199°:

0·0955 gave 0·2066 CO_2 and 0·0358 H_2O. C = 59·0; H = 4·1.

$C_{13}H_{10}O_4S$ requires C = 59·5; H = 4·1 per cent.

The acid is readily soluble in cold ether or alcohol, and sparingly so in cold water. This substance exhibits a characteristic behaviour when its aqueous solution is warmed with concentrated aqueous ferric chloride. The red, crystalline precipitate which is then formed appears to be a ferric salt of the corresponding quinone; but analysis showed that it is of complex composition.

2′-*Carboxy*-2 : 5-*dimethoxydiphenyl Sulphide*, $C_6H_3(OMe)_2\cdot S\cdot C_6H_4\cdot CO_2H$.

A solution of one molecular proportion of the dihydroxy-acid in methyl alcohol which contained an excess of sodium methoxide

was mixed with about three molecular proportions of methyl sulphate. The mixture was subsequently heated on the water-bath, and finally the alcohol was removed by evaporation. The residue was treated with cold aqueous sodium hydroxide, and the insoluble portion was removed by filtration. The filtrates were acidified, and the precipitate was collected and well washed with warm water. The product was finally recrystallised from alcohol, when the required acid was obtained in colourless prisms:

0·1056 gave 0·2399 CO_2 and 0·0487 H_2O. C = 61·9; H = 5·1.

$C_{15}H_{14}O_4S$ requires C = 62·0; H = 4·8 per cent.

When heated, the substance shrinks at about 190°, and finally melts at 195°.

1:4-*Dihydroxythioxanthone*, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{-S-}>C_6H_2(OH)_2$.

A solution of carboxydihydroxydiphenyl sulphide in sulphuric acid was kept overnight at the atmospheric temperature. It was then poured on crushed ice, when the required substance was precipitated in an impure condition. This was collected, washed with water, and then exhaustively extracted with hot alcohol. When cold, the united extracts deposited dihydroxythioxanthone in the crystalline state; but the material tenaciously retained a considerable quantity of sulphuric acid. The further purification of the product was effected by repeated boiling with water until the acid could no longer be detected in the solution. Finally, the substance was recrystallised from alcohol, when it was obtained in deep orange prisms, which melted at 289°, and were sparingly soluble in hot water or common organic media:

0·1866 gave 0·4388 CO_2 and 0·0524 H_2O. C = 64·1; H = 3·1.

$C_{13}H_8O_3S$ requires C = 63·9; H = 3·2 per cent.

The alkali salts of this substance are crimson, but, owing to the ease with which they are oxidised in alkaline solution, they were not isolated in a pure condition. Attempts were made by oxidation to obtain the corresponding quinone, but with the three or four oxidising agents employed the products were difficult to purify, and appeared to consist of polyhydroxy-derivatives.

1:4-*Dimethoxythioxanthone*, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{-S-}>C_6H_2(OMe)_2$.

(*a*) The dimethoxy-derivative of carboxydiphenyl sulphide was treated with sulphuric acid as described above. The product obtained by mixing the acid solution with water was collected, and, after being washed in order to remove excess of acid, was treated

with dilute aqueous sodium hydroxide. The insoluble residue was finally recrystallised from hot alcohol, in which it is moderately soluble.

1 : 4-*Dimethoxythioxanthone* forms bright orange prisms, which melt at 195°, and readily dissolve in sulphuric acid, giving a solution of characteristic red colour:

0·1019 gave 0·2460 CO_2 and 0·0405 H_2O. C = 65·8; H = 4·4.

$C_{15}H_{12}O_3S$ requires C = 66·1; H = 4·4 per cent.

(*b*) The condensation of *o*-dithiobenzoic acid and the dimethyl ether of quinol was carried out by the same process as that employed, and elsewhere described, for the synthesis of other thioxanthone derivatives of a similar type (Marsden and Smiles, this vol., p. 1353). In order to obtain good yields it is important to employ a large excess of the quinol ether and to moderate the temperature of condensation. The product was purified in the usual manner, when it was obtained in orange prisms, melting at 194—195°. A mixed melting point showed that the substance was identical with that obtained by the method described in the foregoing paragraph.

In conclusion, we desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed the expenses of this research.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE, LONDON.

CLXXV.—*Contributions to the Chemistry of the Terpenes. Part IX. The Oxidation of Camphene with Hydrogen Peroxide.*

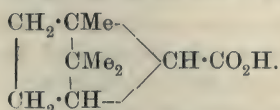
By GEORGE GERALD HENDERSON and MAGGIE MILLEN JEFFS SUTHERLAND, B.Sc., Carnegie Research Scholar.

A THIRTY per cent. aqueous solution of hydrogen peroxide was recently used by one of us (Henderson and Boyd, Trans., 1910, **97**, 1659) as an oxidising agent for various cyclic compounds with satisfactory results, and we have now begun to study the action of this reagent on the terpenes, in the hope that its comparatively mild action, under suitable conditions, would not lead to any of these perplexing changes in molecular structure to which the terpenes in general are peculiarly liable. Camphene, which was selected for

the first experiments, was found to undergo oxidation readily when exposed to the action of hydrogen peroxide under the conditions described in this paper, and to yield a mixture containing a number of different oxidation products, some of which were acids, whilst some were neutral compounds. The chief ingredient of the mixture of acids was a saturated monobasic *acid* of the formula $C_9H_{15}{\cdot}CO_2H$, which was obtained as a crystalline solid, melting at 95°; much smaller quantities of two other acids, one a crystalline solid which melts at about 70°, and the other an oily liquid which boils at 153°/20 mm., were also present. The two latter compounds have not yet been further investigated as their separation is difficult, and the quantity in our hands is unfortunately small. Among the neutral products of oxidation the ketone camphenilone, $C_9H_{14}O$, is present in largest proportion, but in addition to this the mixture contains iso*camphenilanaldehyde*, $C_9H_{15}{\cdot}CHO$, a *compound* which appears to have the formula $C_9H_{16}O_2$, and when heated with phthalic anhydride yields the *acid phthalate* of an *alcohol* of the formula $C_9H_{16}O$, a very small quantity of camphene glycol, $C_{10}H_{16}(OH)_2$, and a trace of a crystalline solid, which melts at about 69°.

The acid of melting point 95°, for which we propose the name *camphylic acid*, was converted into its *chloride*, $C_9H_{15}{\cdot}COCl$, which, when heated with bromine, gave the *chloride* of *bromocamphylic acid*, $C_9H_{14}Br{\cdot}COCl$. The free acid, $C_9H_{14}Br{\cdot}CO_2H$, obtained by treatment of its chloride with water, yielded *hydroxycamphylic acid*, $C_9H_{14}(OH){\cdot}CO_2H$, when heated with aqueous sodium carbonate. The hydroxy-acid did not yield a ketone on oxidation with lead peroxide, and therefore does not contain a tertiary hydroxyl group in the α-position, as is the case with the isomeric camphenylic acid.

When heated with acetic anhydride, camphylic acid is transformed into the isomeric *iso*camphenilanic acid, which was first obtained by the action of hot strong nitric acid on camphenilanic acid (Bredt and Jagelki, *Annalen*, 1900, **310**, 112). The two latter acids are almost certainly stereoisomerides, and there is little doubt that their constitution may be represented by the formula:



Since camphylic acid cannot have this formula, its conversion into *iso*camphenilanic acid must be accompanied by a molecular rearrangement. The constitution of camphylic acid has not been determined, but probably its nucleus is different from that of

camphene. If, as appears to be the case, the molecule of camphene contains the group $>C\colon CH_2$, oxidation would lead to the formation of camphenilanic (or *iso*camphenilanic) acid, and not of camphylic acid, unless a certain rearrangement took place under the influence of the oxidising agent.

*iso*Camphenilanic acid itself is not found among the products of the oxidation of camphene by hydrogen peroxide, although its aldehyde is present in considerable quantity. This leads to the conclusion that hydrogen peroxide is not an active oxidising agent for aldehydes, at least under the conditions which prevailed in our experiments. *iso*Camphenilanaldehyde is very similar in properties to camphenilanaldehyde, with which it is isomeric, and which was obtained by Bredt and Jagelki (*loc. cit.*) as the sole product of the oxidation of camphene with chromyl chloride. On exposure to air, however, the former is oxidised rapidly and completely to *iso*camphenilanic acid (m. p. 118°), whilst the latter yields camphenilanic acid. Both aldehydes appear to form the same semicarbazone, and this compound must really be a derivative of the *iso*aldehyde, because when it is decomposed by treatment with dilute acids it is the latter that is regenerated.

The compound $C_9H_{16}O_2$ is a remarkable one, if its composition be that indicated by the results of analysis, but at present we cannot do more than record its behaviour. It does not react with alkalis, or semicarbazide hydrochloride, or phenyl carbimide, or benzoyl chloride, but is readily oxidised to camphenilone by potassium permanganate, and, as already stated, can be converted into an alcohol, $C_9H_{16}O$, by heating with phthalic anhydride and subsequent hydrolysis of the ester thus produced. The alcohol, which was obtained in crystals, melting at 94°, is apparently isomeric with camphenilol, the secondary alcohol corresponding with camphenilone, but its constitution has not been determined.

Camphenilone has already been obtained from camphene in several different ways, but the direct formation of this compound, and of *iso*camphenilanaldehyde and camphene glycol, through the action of hydrogen peroxide is of interest, because it affords confirmation of the view that the nucleus of each of these substances is the same as that of camphene itself.

We are now engaged in examining the action of hydrogen peroxide on other terpenes, and hope to communicate our results to the Society before long.

Experimental.

Oxidation of Camphene, and Separation of the Acids Produced.—A number of preliminary experiments were made in order to

determine the most favourable conditions for oxidation, and the method ultimately adopted was to add the necessary quantity of a 30 per cent. aqueous solution of hydrogen peroxide to a solution of camphene in four times its weight of glacial acetic acid, and to heat the mixture at about 60° under a reflux condenser. At this temperature the oxidation of the camphene proceeds slowly, and requires several days for completion, but a higher temperature is not advantageous, for although the reaction is accelerated, there is at the same time considerable loss of hydrogen peroxide through decomposition. If smaller proportions of acetic acid are used, some of the camphene remains intact, even after prolonged heating. The quantity of hydrogen peroxide added was varied in different experiments, but with the sole result that the relative proportions of the oxidation products showed corresponding variations, whilst their nature was not affected. When one molecular proportion of the oxidising agent was used for each molecular proportion of camphene, some of the hydrocarbon escaped oxidation, and only a very small quantity of acids was found among the products. When the proportion of hydrogen peroxide was increased to two or three molecules for each molecule of camphene, the oxidation of the latter was practically complete, and the products contained proportionately larger quantities of acids. On the whole, the best results were obtained by taking three molecules of the peroxide for one molecule of camphene.

The oxidation was judged to be complete when no sublimation of camphene into the tube of the condenser was observed. Sodium carbonate was then added to the liquid, which had acquired a yellow colour, until nearly all the acetic acid was neutralised, and a yellow, oily liquid which separated was extracted by repeated agitation of the mixture with ether. The aqueous solution was acidified with dilute sulphuric acid and thoroughly extracted with ether, and from the ethereal extract a small quantity of acids was obtained. The ethereal solution of the bulk of the oxidation product was washed with water, dried, and the oily liquid which remained after removal of the ether by distillation was warmed on the water-bath with aqueous sodium carbonate until no more passed into solution. The alkaline liquid, when cool, was shaken several times with ether in order to remove the neutral substances which remained undissolved, which constituted the greater part of the whole product, and was then acidified with dilute sulphuric acid. The precipitated acids, together with the small quantity which remained in solution, were extracted with ether, and, after the extract had been washed with water and dried, were recovered on distilling off the ether in the form of an oily liquid,

which gradually became crystalline. The separation of the acids present in this mixture was very troublesome and tedious because of their great solubility in all the usual organic solvents, but ultimately, by repeated recrystallisation from light petroleum and subsequently from methyl alcohol, we succeeded in isolating three acids. The least soluble portion, which constituted the bulk of the mixture, was a solid melting at 93—94°; the second fraction was also a solid, melting at about 70°, and the most easily soluble part was an oily liquid, which boils at 153°/20 mm. Only small quantities of the two latter acids were obtained, and their further examination was postponed from lack of material.

The principal acid, $C_9H_{15}\cdot CO_2H$, which may be called *camphylic acid*, when finally purified by crystallisation from water and from light petroleum successively, melted at 95°. It is extremely easily soluble in alcohol, ether, light petroleum, or other usual organic solvents, very sparingly so in hot, and hardly at all in cold, water, and it has a great tendency to form supersaturated solutions in methyl alcohol or light petroleum. From the latter solvents it crystallises in well developed, colourless, lustrous prisms, which, if formed slowly, may be a centimetre or more in length, and from water or dilute methyl alcohol it separates in delicate needles. It volatilises, but slowly, in a current of steam. Towards bromine or potassium permanganate, it behaves as a saturated compound. When heated on the water-bath with a strongly alkaline solution of potassium permanganate, it is slowly attacked, but no oxidation product other than carbon dioxide was identified. It remains unchanged, even after prolonged heating with nitric acid of concentrations varying from 10 to 50 per cent.:

0·2475 gave 0·6472 CO_2 and 0·2169 H_2O. C = 71·3; H = 9·8.
0·1864 „ 0·4850 CO_2 „ 0·1622 H_2O. C = 71·0; H = 9·7.
$C_{10}H_{16}O_2$ requires C = 71·4; H = 9·6 per cent.

The *sodium* salt separates from water, in which it is readily soluble, in small, colourless prisms. The *ammonium* salt, which also is easily soluble in water, was obtained as a colourless, crystalline powder by passing ammonia into a solution of the acid in dry ether. The *silver* salt, $C_9H_{15}\cdot CO_2Ag$, was precipitated as a white, finely crystalline solid on addition of silver nitrate to an aqueous solution of the ammonium salt. It is practically insoluble in water, and darkens slowly when exposed to light. Analysis of this salt confirmed the results obtained with the acid:

0·1432 gave 0·2294 CO_2, 0·0814 H_2O, and 0·0565 Ag. C = 43·7; H = 6·3; Ag = 39·5.
$C_{10}H_{15}O_2Ag$ requires C = 43·6; H = 5·6; Ag = 39·3 per cent.

The first analyses of the acid, which were made on a specimen crystallised from water and not thoroughly dried, gave results which suggested that it might be campholic acid, $C_{10}H_{18}O_2$; moreover, like the latter, the new acid is precipitated, although very slowly, when carbon dioxide is passed through a cold aqueous solution of its sodium salt. In order to settle the point, an attempt was made to prepare the anhydride, which can be obtained from campholic acid. A few grams of the acid were boiled for about an hour under a reflux condenser with a slight excess of acetic anhydride, and the mixture then poured into a large quantity of water, which was subsequently shaken several times with ether. The ethereal solution was washed and dried, the ether removed by distillation, and the residue dissolved in hot light petroleum, in which it was considerably less soluble than the original acid. On cooling the solution, clusters of small, colourless prisms separated which, when dry, melted at 118°, and on treatment with sodium carbonate proved to be crystals of an acid. The melting point of this acid was not changed when it was mixed with *iso*camphenilanic acid, $C_9H_{15}\cdot CO_2H$, which also melts at 118°, and analysis confirmed the conclusion that it was nothing but the latter. (Found, C=71·5; H=9·5. Calc., C=71·4; H=9·6 per cent.)

This experiment showed that camphylic acid is transformed into the isomeric *iso*camphenilanic acid when heated with acetic anhydride. No such transformation is brought about when the acid is crystallised repeatedly from alcohol, water, or light petroleum, or when it is heated for hours at 150°, or when it is distilled under diminished pressure.

Preparation of Bromo- and Hydroxy-camphylic Acids.—The acid was added in small portions to a mixture of the calculated quantity of phosphorus pentachloride with light petroleum contained in a flask under a reflux condenser, the solution was heated to complete the reaction, and then distilled fractionally under diminished pressure. After the solvent and the phosphoryl chloride had passed over, the *chloride* of the acid, $C_9H_{15}\cdot COCl$, distilled at 110°/17 mm. It is a colourless, viscous liquid, with a pungent but not unpleasant odour, which fumes in moist air. By heating this compound with a slight excess of bromine in a sealed tube at about 90° for several hours, the *chloride* of the bromo-acid, $C_9H_{14}Br\cdot COCl$, was obtained as a heavy, viscous liquid, which, when well stirred with water, was slowly converted into the crystalline *bromocamphylic acid*, $C_9H_{14}Br\cdot CO_2H$. The acid was collected, dried, and crystallised, first from methyl alcohol, and then from light petroleum. It forms small, lustrous prisms, melts at 210°,

and is very readily soluble in alcohol or ether, sparingly so in light petroleum, and insoluble in water:

0·2002 gave 0·1524 AgBr. Br = 32·3.

$C_{10}H_{15}O_2Br$ requires Br = 39·4 per cent.

On one occasion, in brominating the chloride of camphylic acid, the temperature was accidentally allowed to rise to about 200°. When the product was treated with water a neutral compound, which contained bromine, and a bromo-acid, which melted at 204—205°, were obtained. The latter was identified as bromo*iso*camphenilanic acid, and it follows that, at the high temperature of the experiment, the chloride of bromocamphylic acid must have been transformed into the chloride of bromo*iso*camphenilanic acid.

Hydroxycamphylic acid, $C_9H_{14}(OH)\cdot CO_2H$, was prepared by heating the bromo-acid for some time with excess of aqueous sodium carbonate, and acidifying the alkaline solution, when cool, with dilute sulphuric acid. The crystalline acid which separated was collected on a filter, and the filtrate was extracted repeatedly with ether in order to obtain the portion that remained in solution. In order to remove a small quantity of resinous matter with which it was contaminated, the acid was converted into its *sodium* salt, which was obtained in colourless prisms when the solution was concentrated. The salt was redissolved in water, in which it is fairly readily soluble, and decomposed by addition of sulphuric acid, and the hydroxy-acid was finally purified by successive crystallisations from water and from light petroleum. From the latter solvent it separates in small, lustrous prisms, which melt at 245°. It is very easily soluble in alcohol or ether, fairly so in water or light petroleum:

0·2001 gave 0·4750 CO_2 and 0·1622 H_2O. C = 64·7; H = 9·0.

$C_{10}H_{16}O_3$ requires C = 65·2; H = 8·7 per cent.

In order to gain more information as to its constitution, a mixture of the hydroxy-acid with a little water and about four times its weight of lead peroxide was distilled in a current of steam. The distillate contained a crystalline, insoluble solid, which was collected and pressed in porous paper. It melts at 145°, and has an odour of geraniums; it has the character, not of a ketone, but of an acid. Lack of material prevented further examination of this compound.

Separation of iso*Camphenilanaldehyde*.—The ethereal solution of that portion of the original oxidation product which had not been dissolved by aqueous sodium carbonate was washed with water, dried, and after removal of most of the ether the residual liquid

was mixed with an equal volume of a saturated solution of sodium hydrogen sulphite. Almost at once a "bisulphite compound" began to separate in small, pearly leaflets. After some time this compound was collected, and washed with a very little alcohol, in which it is fairly readily soluble, and with ether. The part of the oily product which had not combined with sodium hydrogen sulphite was extracted from the aqueous filtrate with ether, and treated with fresh quantities of the reagent until no more crystals of the bisulphite compound were formed. The greater proportion of the mixture of neutral oxidation products remained unattacked, and was examined in the manner described below.

iso*Camphenilanaldehyde*, $C_9H_{15}\cdot CHO$, was obtained by mixing the bisulphite compound with excess of aqueous sodium carbonate, and passing a current of steam through the solution. The aldehyde distilled quickly with steam, and collected in the receiver in soft, crystalline masses. Being extremely easily soluble in alcohol or ether, it is not easily purified by crystallisation from these solvents, and was therefore converted into its semicarbazone, which, after recrystallisation until its melting point was constant, was decomposed by warming with the calculated quantity of dilute sulphuric acid. The liquid was cooled, and the aldehyde collected, well washed with water, and quickly dried by pressure in porous paper. It forms waxy, colourless crystals, which melt at 69—70°, and, like other terpene aldehydes, has a strong, peculiar odour. It is very easily soluble in alcohol, ether, or light petroleum, but insoluble in water, and it readily volatilises in a current of steam. On exposure to air, it oxidises quickly and completely to *iso*camphenilanic acid. Altogether it closely resembles the isomeric camphenilanaldehyde.

The *semicarbazone* of *iso*camphenilanaldehyde,

$$C_9H_{15}\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2,$$

crystallises from methyl alcohol in small, lustrous prisms, which melt at 191—192°. It dissolves readily in hot, rather sparingly so in cold, methyl alcohol:

0·1960 gave 32·8 c.c. N_2 (moist) at 19° and 766 mm. N=20·1.

$C_{11}H_{19}ON_3$ requires N=20·1 per cent.

The semicarbazone prepared from camphenilanaldehyde melts at the same temperature as the compound derived from *iso*camphenilanaldehyde, and so does a mixture of the two compounds, which are thus shown to be identical.

The crystals of the acid produced by exposure of *iso*camphenilanaldehyde to the air was found to melt at 108—112° after pressure in porous paper, and at 118° after crystallisation from light petroleum, from which it separates in clusters of small, colourless

prisms. The melting point was not changed by further crystallisation, and a mixture of the acid with a specimen of *iso*camphenilanic acid, which had been prepared from camphene by Bredt's method, also melted at 118°. Hence the acid was proved to be *iso*camphenilanic acid, and the aldehyde from which it was formed by spontaneous oxidation in air at the ordinary temperature must be *iso*camphenilanaldehyde.

Separation of Camphenilone.—The mixture of neutral oxidation products, which remained after extraction of the acids with sodium carbonate and of *iso*camphenilanaldehyde with sodium hydrogen sulphite, was a viscous liquid, brown in colour, and with a strong odour. On distillation under diminished pressure in an atmosphere of dry carbon dioxide, slight decomposition took place, a small quantity of a dark resinous substance being left in the flask, but the bulk passed over into the receiver. After repeated distillation the mixture was separated into three liquid fractions, which boiled at 85—88°, 94—100°, and about 250° respectively under 15 mm. pressure.

The chief fraction, that of lowest boiling point, was a colourless, oily liquid, which could not be induced to crystallise, although its characteristic odour suggested that it was the ketone camphenilone, $C_9H_{14}O$. Analysis indicated that it was a mixture of camphenilone with a little of another substance, and on treatment of a sample with semicarbazide hydrochloride the greater part was quickly converted into a crystalline semicarbazone, but a small quantity of an oily liquid remained unattacked by the reagent. Accordingly, the rest of the fraction was mixed with semicarbazide hydrochloride and potassium acetate, with the necessary quantity of methyl alcohol and water to form a clear solution, enough of the reagent being used to react with the whole of the substance. The semicarbazone, which quickly separated, was collected, and the mother liquor was diluted with water and distilled with steam. The small quantity of oily liquid which distilled with steam was added to the second fraction.

The semicarbazone crystallised from methyl alcohol, in which it is readily soluble, in colourless needles, which melted at 224—225°, the melting point of camphenilonesemicarbazone. Analysis gave a corresponding result. (Found, N = 21·9. Calc., N = 21·7 per cent.)

The pure ketone was obtained by warming the semicarbazone with the calculated quantity of dilute sulphuric acid. On cooling, a solid separated, which was collected, washed with water, dried, and crystallised from ether, from which it separated in colourless plates, melting at 40°. The ketone had a strong odour, was very easily soluble in alcohol, and readily volatile in steam, and behaved

as a saturated compound towards bromine and towards potassium permanganate. Further proof of its identity with camphenilone was obtained by preparing the oxime, which separated from ether in small, colourless crystals, melting at 105—106°, and very easily soluble in alcohol, chloroform, or light petroleum. These are the properties of campheniloneoxime.

Separation of the other Neutral Products.—The quantity of the second fraction (b. p. 94—100°/15 mm.) was much smaller than that of the first. It was first treated with semicarbazide hydrochloride in order to remove any remains of camphenilone, and, after separation from the mother liquor by steam distillation, was fractionated several times under diminished pressure. When purified in this way the product was a colourless, oily liquid with a faint, pleasant odour, which distilled at 94—96°/14 mm. It was analysed with the following results:

0·1754 gave 0·4460 CO_2 and 0·1672 H_2O. C = 69·3; H = 10·5.
0·1754 „ 0·4430 CO_2 „ 0·1678 H_2O. C = 68·9; H = 10·6.
$C_9H_{16}O_2$ requires C = 69·2; H = 10·3 per cent.

This *compound* is easily oxidised by alkaline potassium permanganate, yielding a substance which has the physical properties of camphenilone, and from which a semicarbazone with the same melting point as camphenilonesemicarbazone was prepared. The compound was apparently indifferent to the action of hot aqueous sodium hydroxide, did not react with phenylcarbimide, and was not affected when treated with benzoyl chloride in presence of pyridine. It was converted into the *acid phthalate* of an alcohol, $C_9H_{16}O$, in the following manner. After heating the compound for some time at 150—180° with twice its weight of phthalic anhydride, the product was poured into a beaker containing crushed ice, and sodium carbonate was added until nothing more passed into solution. The alkaline solution was filtered, agitated with ether, acidified with dilute sulphuric acid, and then thoroughly extracted with ether. The ethereal solution was washed and dried, and after removal of the ether the residue was again treated with sodium carbonate, etc., as before. The ester, thus freed from phthalic acid, was finally purified by crystallisation from a mixture of ether and light petroleum, from which it separates in lustrous prisms, which melt at 163—164°. It is very readily soluble in alcohol or ether, very sparingly so in light petroleum or chloroform, and is dissolved by aqueous sodium carbonate with formation of a soluble sodium salt:

0·1134 gave 0·2922 CO_2 and 0·0746 H_2O. C = 70·3; H = 7·3.
$C_{17}H_{20}O_4$ requires C = 70·8; H = 6·9 per cent.

The *alcohol*, $C_9H_{16}O$, was prepared by warming the ester with aqueous sodium hydroxide, and distilling the liberated alcohol in a current of steam. It collected in the receiver in the form of a white, waxy, crystalline solid, with an odour somewhat like that of camphor, and, when dry, melted at 94—95°. It is very readily soluble in alcohol or ether, and practically insoluble in water:

0·1546 gave 0·4348 CO_2 and 0·1632 H_2O. C=76·7; H=11·7.
0·1690 „ 0·4732 CO_2 „ 0·1722 H_2O. C=76·4; H=11·6.
$C_9H_{16}O$ requires C=77·1; H=11·4 per cent.

This alcohol, although apparently of the same composition, appears to be different from camphenilol, the alcohol corresponding with camphenilone, for the latter melts at 84°, and its acid phthalic ester at 148°. The nature of the compound from which the alcohol was derived has not been determined.

Only a very small quantity was obtained of the highest fraction (b. p. about 250°/15 mm.) of the neutral oxidation product. It was an extremely viscous liquid, with a yellow colour, and appeared to contain traces of several compounds. We succeeded in isolating a very small quantity of camphene glycol, $C_{10}H_{16}(OH)_2$, and a still smaller quantity of a crystalline compound, which melted at about 69°. This substance forms small, lustrous plates, and is very sparingly soluble in methyl alcohol, fairly readily so in ether.

The preliminary work connected with this research was done by Mr. W. Dickson, A.I.C., who was prevented from completing it by the acceptance of an appointment.

We are indebted to the Carnegie Trust for a grant in aid of the expense of this work, and gladly take this opportunity of expressing our thanks.

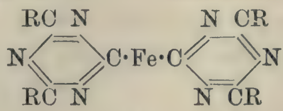
CHEMISTRY DEPARTMENT.
THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

CLXXVI.—*The Constitution of the Organic Ferrocyanides.*

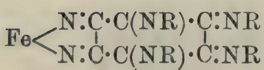
By ERNALD GEORGE JUSTINIAN HARTLEY.

IN two previous communications (Trans., 1910, **97**, 1066 and 1725) the author described some new organic derivatives of hydroferrocyanic acid formed, in the first place, by the action of methyl sulphate on dry potassium ferrocyanide. From the compounds so produced, which are acid and neutral salts of a hexamethylferro-

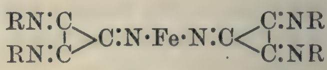
cyanogen base, by a series of further operations tetramethyl ferrocyanide was prepared. Owing to the uncertainty that still exists as to the constitution of the ferrocyanides, it seemed interesting to study the decomposition products of one or two of these substances in order to throw some light on the subject if possible. The numerous formulæ which have been proposed from time to time for the ferrocyanides may be placed in two classes. The first includes those in which the usual structural conceptions of organic chemistry are adopted:



(I.)



(II.)



(III.)

(I), an example of this class, appears in several standard textbooks of organic chemistry, and was provisionally employed by the author in the papers referred to above. It has apparently been suggested owing to the well-known tendency of the cyanogen radicle to form the stable tricyanogen ring rather than from any specific chemical behaviour of the ferrocyanides.

Further examples are (II) put forward by Friedel (*Compt. rend.*, 1887, **104**, 995), but admitted by him to be not wholly satisfactory, and (III), proposed by Browning (Trans., 1900, **77**, 1238). The latter seems in many respects to represent very well the properties of the ferrocyanides, especially their relationship to the nitroprussides, but it does not appear to have been very widely accepted by organic chemists.

It will be noticed that in (I) the metallic radicles are combined directly with carbon atoms, whilst in (II) and (III) they are attached to nitrogen.

The second class consists of formulæ deduced from various modifications of Werner's so-called co-ordination theory.

It would not be convenient in this communication to enter into a discussion as to the merits of these systems, but reference should be made to two papers by Briggs (Trans., 1908, **93**, 1571, and this vol., p. 1019), in which he applies his own development of the theory to explain the existence of the α- and β-ferricyanides described by Locke and Edwards (*Amer. Chem. J.*, 1899, **21**, 193, 413), and the similar α- and β-ferrocyanides discovered quite recently by himself (*loc. cit.*).

It is not claimed that any definite conclusion can be drawn

from the following experiments as to the general configuration of the molecule, but the arguments in this paper are based on the supposition, favoured by the author, that the ordinary structural theory of organic chemistry can at present be applied to this class of compounds more advantageously than Werner's or any allied system. On this assumption it is demonstrated fairly conclusively that the organic ferrocyanides, at any rate, must be represented by a formula in which the alkyl groups are shown as directly attached to nitrogen. Whether the free acid and its salts are similarly constituted cannot yet be asserted.

It is well known that when metallic ferrocyanides are decomposed by concentrated sulphuric acid, the nitrogen is converted into an ammonium salt, and it seemed probable that the organic ferrocyanides would behave in a similar manner.

The nitrogen would then presumably be found entirely in the form of an ammonium salt if a formula similar to (I) is the correct one, whereas if the methyl groups are attached directly to nitrogen the decomposition should result in the production of some methylammonium derivatives.

In fact, Freund, in his original paper on tetraethyl ferrocyanide, prepared from silver ferrocyanide and ethyl iodide (*Ber.*, 1888, **21**, 931), observed that this substance gave off an *iso*cyanide on heating, and that both ethylamine and ammonium sulphates were found in the residue after heating with concentrated sulphuric acid, and these results were confirmed later by Browning (*loc. cit.*).

Experiments have now been carried out on the decomposition, both of tetramethyl ferrocyanide and also of one of the hexamethyl derivatives, namely, hexamethylferrocyanogen dihydrogen sulphate, $(CH_3)_6FeC_6N_6H_2(SO_4)_2$, since of all the series the latter is most readily obtained pure, and it was hoped that the position of the six methyl groups might be elucidated.

About 0·5 gram of pure tetramethyl ferrocyanide was gradually heated with thirty drops of concentrated sulphuric acid in a platinum crucible until white fumes just began to appear. After keeping at this temperature for several hours the crucible was cooled and the contents examined.

The iron was found to be almost entirely converted into ferric sulphate, which is only very slowly soluble in water when anhydrous. A little water was added, the solution filtered from the iron salt, and a drop of the liquid was tested with platinic chloride, when a precipitate was immediately formed, which was seen under the microscope to consist of a mixture of octahedra and hexagonal plates evidently of ammonium and methylamine platinichlorides respectively.

To the rest of the solution excess of platinic chloride was added, and the precipitate was collected, washed with dilute alcohol, dried at 100°, and the platinum determined:

0·3132 gave 0·1340 Pt. Pt=42·78.

Ammonium platinichloride requires Pt=43·92.

Methylamine platinichloride requires Pt=41·31 per cent.

The percentage of platinum was, as expected, between these two values, but owing to the greater solubility of the methylamine salt it is not possible to calculate the proportion of the two constituents.

A similar experiment was next performed with the hexamethyl compound, the heating being conducted in exactly the same way as above. In order to obtain some evidence as to how far the decomposition is complete under these conditions, the iron was determined in one portion. For this purpose water and a little dilute hydrochloric acid were added to the contents of the crucible, which was allowed to remain until all the ferric salt had dissolved. The iron was then precipitated with ammonia in the usual way, and weighed:

0·6247 gave 0·1040 Fe_2O_3. Fe=11·65.

$C_{12}H_{20}N_6Fe(SO_4)_2$ requires Fe=11·28 per cent.

Since the iron is not precipitated by ammonia from a solution of the original salt, it is evident that the decomposition was complete, at least so far as detaching the iron from the rest of the molecule.

A second portion of salt was similarly treated, and the platinichloride examined. It was seen under the microscope to consist entirely of hexagonal plates, none of the octahedra of the ammonium salt being observed.

A determination of platinum confirmed this. (Found: Pt=41·47. Calc. for methylamine platinichloride, Pt=41·31 per cent.)

A further experiment was made on the decomposition of the hexamethyl salt with sodium hydroxide solution.

0·2 Gram of salt was heated in a distilling flask with 100 c.c. of 10 per cent. aqueous sodium hydroxide. Decomposition immediately became apparent, a strongly alkaline vapour and an *iso*cyanide being given off, whilst the liquid turned brown, and finally deposited a brownish-black precipitate, probably a mixture of ferrous and ferric hydroxides, since it dissolved in hydrochloric acid, and the solution so obtained gave a blue precipitate, both with potassium ferro- and ferri-cyanide.

The contents of the flask were boiled until about two-thirds of the liquid had passed over, the evolved vapour being condensed in a vessel containing dilute hydrochloric acid, which would convert the *iso*cyanide into an amine salt, and also combine with any free

amine or ammonia if present. When the distillation was stopped, an *iso*cyanide was still being given off in quantity, but it was not possible to continue the boiling without risk of the liquid bumping over. The distillate was evaporated to dryness to remove excess of hydrochloric acid, and the residue was dissolved in a small quantity of water and treated with an excess of platinic chloride and a fair quantity of alcohol.

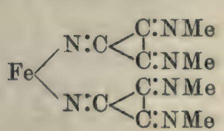
The precipitate, when washed with alcohol and dried, weighed 0·4117 gram, which corresponds with about 72 per cent. of the total nitrogen in the salt taken.

A small portion was examined microscopically, and seen to be free from the octahedra of the ammonium salt.

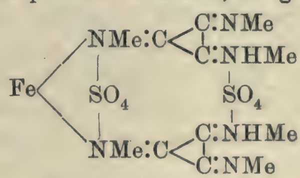
The percentage of platinum again agrees with the ordinary errors of analysis with that required for the methylamine salt (Found, Pt=41·49. Calc., Pt=41·31 per cent.), so that these values, together with the microscopic examination of the platinichlorides, may be taken to prove that no ammonium salt was present.

The fact that the nitrogen in the hexamethyl salt after two completely different methods of decomposition is only found as a methylamine derivative, leads to the conclusion that all the six methyl groups are attached to nitrogen atoms, and consequently in the tetramethyl compound the four methyl groups are probably similarly combined, the two remaining nitrogen atoms in this case forming the ammonium sulphate found after decomposition with sulphuric acid.

Applying Browning's formula to these substances as the best of the ordinary structural formulæ at present available, we get:



Tetramethyl ferrocyanide.



Hexamethylferrocyanogen dihydrogen sulphate.

the position of the H_2SO_4 in the acid salt being uncertain.

It may finally be suggested that, if the metallic ferrocyanides are constituted similarly to the tetramethyl compound, the α- and β-forms referred to above may be cases of geometrical isomerism due to nitrogen atoms doubly linked to carbon.

In conclusion, I wish to express my thanks to Lord Berkeley, in whose laboratory these experiments have been carried out, for his help and interest in the work.

Foxcombe Laboratory,
Nr. Oxford.

CLXXVII.—*The Osmotic Pressure and Conductivity of Aqueous Solutions of Congo-red, and Reversible Membrane Equilibria.*

By Frederick George Donnan and Albert Buckley Harris.

The object of the work described in this paper was to make a somewhat detailed examination of the molecular state of Congo-red in aqueous solution by means of measurements of osmotic pressure and electrical conductivity, and to investigate the effects of certain electrolytes on these properties.*

Congo-red, the disodium salt of diphenylbisazonaphthylaminesulphonic acid, is known to possess colloidal properties in aqueous solution. For example, it does not diffuse, or only very slowly, through a membrane of parchment paper, thus rendering the measurement of its osmotic pressure possible with a diaphragm of this sort. W. M. Bayliss (*Proc. Roy. Soc.*, 1909, **81**, *B*, 345) has made several measurements of the osmotic pressure of Congo-red, his apparatus being a modification of that used by Moore and Roaf (*Bio-Chem. J.*, 1907, **2**, 34). His method consisted in placing Congo-red acid in the osmometer, and adding dilute sodium hydroxide solution to the outside water every twenty-four hours until the latter retained a slight permanent alkalinity. The outside water was then repeatedly changed until no further rise in osmotic pressure occurred. The maximum pressure so obtained was found to vary from 88 to 97 per cent. of the value calculated on the assumption that Congo-red exists in solution as simple, undissociated, and non-aggregated molecules, and from these results Bayliss drew the conclusion that the dye really does exist in solution as simple molecules (M.W. = 696·5). This conclusion, which in itself is rather an unlikely one, will be shown in the course of this paper to be untenable.

Bayliss further showed that the osmotic pressure of Congo-red is lowered by the presence of sodium chloride, sodium hydroxide, and carbon dioxide (carbonic acid).

Since the commencement of the present work † a paper on the osmotic pressure of several colloids has been published by Biltz and von Vegesack (*Zeitsch. physikal. Chem.*, 1909, **68**, 357), among the colloids examined by them being benzopurpurine-4B, a dyestuff

* This work was primarily undertaken as a preliminary study to a similar investigation of the state of soaps in aqueous solution. The osmotic pressures of these solutions are being at present investigated in this laboratory.

† The publication of the present work has been unfortunately delayed for a year, the experiments having been completed in May, 1910.

nearly related to Congo-red in chemical composition. From their experiments they concluded that in the absence of foreign electrolytes benzopurpurine-4B exerts a negligibly small osmotic pressure.* They remarked that during dialysis the solution undergoes a change, the originally bright red solution becoming brownish-black, and they considered this to be simply a mechanical and not a chemical effect, because by heating the dialysed solution (presumably in a glass vessel) the original appearance of the solution was restored. It was assumed by these authors that no hydrolysis could have taken place, because in a particular experiment in which six litres of water were used as outside liquid, no alkali could be detected therein. With regard to the regeneration of the brownish-black dialysed solution by heating, it is quite possible that, even if (partial) hydrolysis had taken place, the alkali taken up from the glass on heating would have been sufficient to reconvert the substance or substances produced by this partial hydrolysis into the original benzopurpurine salt. Thus it is quite easy to convert a dilute solution of the blue Congo-red acid into the bright red solution of the salt by simply boiling the former for some time (less than half an hour) in an ordinary glass beaker.

Again, the fact that no free alkali was detected by Biltz and von Vegesack in the six litres of outside water can easily be accounted for by the large volume of this outside liquid, and the relatively small amount of alkali to be expected.†

It will be shown in the present paper that in this and similar cases hydrolysis, accompanied by the outward diffusion of free alkali, undoubtedly occurs. Indeed, this phenomenon of what we may call "forced membrane-hydrolysis" is an exceedingly interesting and important one, and must always occur to some extent when an electrolyte with a non-dialysing ion (whether kation or anion) is separated by a suitable membrane from pure water.‡

Experimental.

For the osmotic pressure measurements described in the present paper, an osmometer was employed which was a modified form of that described by Roaf (*Quart. J. Physiol.*, 1910, **3**, 75). A short cylinder of glass 2 cm. long and 3·5 cm. in diameter, provided with

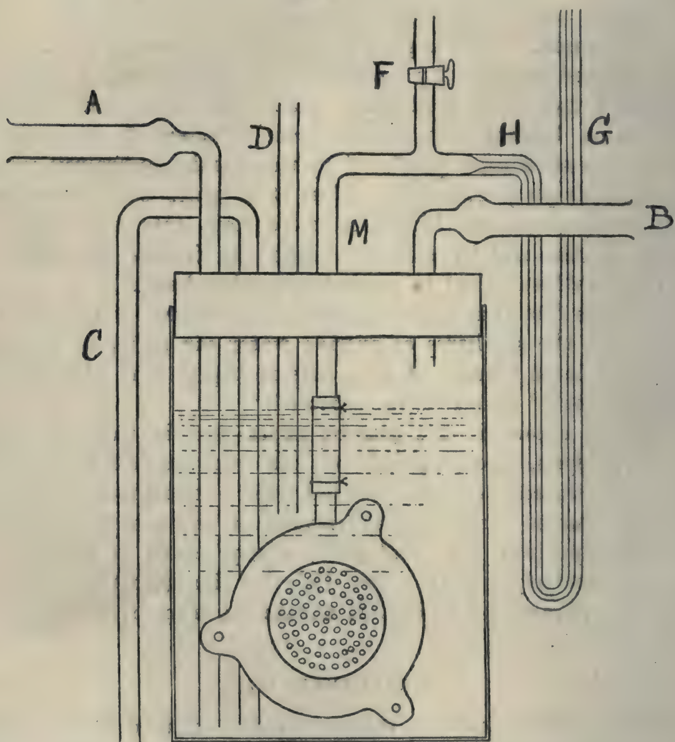
* Some of the erroneous conclusions arrived at by Biltz and von Vegesack have been corrected in a subsequent paper, which will be discussed later (see p. 1575).

† Moreover, unless every precaution was taken to exclude carbon dioxide, a detection of the free alkali which had diffused out by means of phenolphthalein would be very uncertain.

‡ The general theory of the action of membranes in the presence of electrolytes possessing a non-dialysable ion will be discussed in another paper.

a sealed-in side-tube for connexion to the manometer, was closed at either side by parchment-paper diaphragms. These were backed up externally by perforated silver plates, which were tightly pressed against the diaphragms by means of an annular metal framework consisting of two metal rings provided with suitable nuts and screws. A tight joint between the parchment paper and the glass edges of the osmometer vessel was secured by annular rubber washers. The internal volume of the osmometer vessel

FIG. 1.



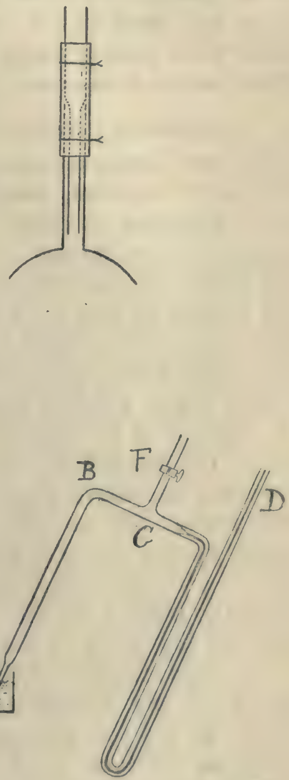
was 20 c.c. Connexion between the latter and the tube leading to the manometer was effected as shown in Fig. 2, the narrowed end of the manometer-tube projecting into the side-tube of the osmometer vessel, the joint being secured by tightly wired rubber pressure-tubing.

The general arrangement is shown in Fig. 1. The osmometer was suspended in a stout cylindrical glass jar of about 1300 c.c. capacity, closed by a large cork, through which passed the tube *M*

leading to the manometer, two soda-lime tubes, A and B, by means of which the entrance of carbon dioxide is prevented, and two tubes, C and D (closed by rubber tubes and screw-clips), for changing the liquid external to the osmometer.

In the manometer HG (internal diameter 1 mm.) mercury was employed as manometric fluid. The side-tube F was employed in the filling and connecting of the manometer, which was carried out as follows. The osmometer vessel, together with the pressure-tubing by means of which it is to be connected to the manometer, is completely filled with the solution to be employed. Mercury is then introduced into the dry inverted manometer through the end A (see Fig. 2), the mercury collecting at the bend B. By now quickly bringing the manometer into its normal position, keeping the end D closed by the finger, the mercury is obtained in the two arms of the capillary pressure gauge without any break, sufficient mercury having been introduced so that in the inclined position shown in Fig. 2 one end of the mercury column can be brought to the position C. The end A being now dipped into the required solution, the latter is drawn into the manometer by suction at F. By now bringing AB into a vertical position after closing the tap F (the end A being still immersed in the solution), the excess of mercury can be run out and the levels brought to any desired position in the pressure-gauge by blowing in at D, the mercury which is driven over collecting in the vessel A, and being replaced by the solution. The manometer and osmometer having been completely filled are joined together in the manner indicated previously. The modelling material "Plasticene" was found to be a very convenient substance for making the cork of the outer cylindrical jar quite air-tight, a thick layer of this material being spread over the whole top of the cork.

FIG. 2.



After the apparatus has been set up, air, free from carbon dioxide, is drawn for a considerable time through the water in the jar by attaching *B* to a filter pump and *A* to a series of long soda-lime tubes. Thoughout all the experiments the presence of carbon dioxide was carefully excluded, for reasons which will appear later.

With regard to the measurement of the osmotic pressure, a correction has obviously to be made for the difference between the level of the outer liquid in the jar and that of the mercury column in the nearer limb of the manometer (the other limb of the manometer was open to the atmosphere). This correction is additive if the water level is below the lower mercury level, and subtractive if the reverse is the case.

Preliminary Series of Measurements of Osmotic Pressure.

The first series of measurements was made with solutions of Grübler's Congo-red, which was found to contain about 30 per cent. of sodium chloride. A litre of distilled water, free from carbon dioxide, formed the external liquid. The same general behaviour was observed in all these experiments. The pressure rose quickly at first, the velocity of increase gradually diminishing. After four to five days the pressure attained a maximum, and then began slowly to decrease. On changing the external water, a further rise in pressure occurred, followed by a slow fall. Succeeding changes of the external water gave rise to the same phenomenon, the increase of pressure becoming, however, rapidly smaller with each successive change of external water. The experiments were carried out at room temperature (17°), and entrance of carbon dioxide carefully prevented. It was found that the original litre of external water contained nearly all the sodium chloride originally present in the Congo-red, the second litre practically removing the whole of the remainder.

The concentration of the Congo-red in the osmometer (after removal of the sodium chloride) was determined by evaporating 10 c.c. of the cell contents at the end of the experiment, and drying to constant weight at 110—115°. The following figures give the results of an osmotic pressure measurement. (Experiment I.):

Time (hours).	Difference of mercury levels (mm.).	Time (hours).	Difference of mercury levels (mm.).
24	88·5	282	125·0
73	105·0	306*	124·0
96	107·5	314	125·0
144	108·0	330*	122·0
234*	105·0	356*	123·0
240	119·0	401	121·0
258	123·0	450	115·0

* Indicates a change of the external water.

Final concentration of Congo-red = 0·578 gram per 100 c.c.

Maximum pressure (corrected for difference of levels) = 136 mm. (125 + 11).

For single undissociated molecules the osmotic pressure would be:

$$22{\cdot}4 \times 760 \times \frac{290}{273} \times \frac{5{\cdot}78}{696{\cdot}5} = 140 \text{ mm.}$$

The observed value is therefore 97 per cent. of this calculated value.*

Two other experiments carried out in a similar manner yielded the following final results:

II.	Concentration of Congo-red	=	0·387 gram per 100 c.c.
	Maximum pressure observed	=	97·0 mm.
	Calculated value	=	100·5 mm.
	Observed value	=	96·5 per cent. of calculated value.
III.	Concentration of Congo-red	=	0·756 gram per 100 c.c.
	Maximum pressure observed	=	185·5 mm.
	Calculated value	=	196·0 mm.
	Observed value	=	95·0 per cent. of calculated value.

These results show a good general agreement with those obtained by Bayliss, in which the Congo-red salt was formed in the osmometer by diffusion of alkali to the blue Congo-red acid. The rise of osmotic pressure observed after each change of external water might be due, as Bayliss supposes, to an increase of "dispersivity" (and therefore presumably of osmotic pressure) of the Congo-red solution, as the sodium chloride diffuses out through the parchment diaphragm, or it might be due to the sodium chloride still present in the osmometer exerting an osmotic pressure before it has time to diffuse out. In order to test the latter explanation, experiments (to be described later) have been made with solutions of pure sodium chloride in the osmometer. The general result of these experiments is that the small amount of sodium chloride remaining in the osmometer, even before the first change of external water, that is, after about seven days, could not cause the rise of pressure observed. This argument assumes an equal concentration of sodium chloride inside the osmometer and in the external water. It will be shown later, however, that after a few days the sodium chloride becomes unequally distributed, that is, its concentration in the external water becomes greater than in the osmometer vessel, thus producing an osmotic pressure opposed to that of the Congo-red. When the external water is changed, this counter-pressure is removed, and so a sensible rise of osmotic pressure

* Throughout this paper, the expression "calculated value" will always refer to that calculated for single undissociated molecules. This method of expressing the results is simply used for the purpose of providing a convenient standard of comparison.

occurs, that is, the true pressure due to the Congo-red present in solution inside the osmometer is observed. That this is probably the true explanation of the phenomenon will appear from the later experiments. It is not necessary, therefore, to suppose that the small concentration of the sodium chloride present in the osmometer exerts any intrinsic action in depressing the osmotic pressure of the Congo-red. This very important matter will be discussed more fully later on.

With regard to the gradual decrease of pressure after a maximum has been attained, this might be attributed to various causes. Sodium chloride might be supposed to be still diffusing slowly from the osmometer, the Congo-red might be undergoing some change of "physical" state, as Biltz and von Vegesack suppose, or a chemical change such as hydrolysis might be occurring. The first hypothesis may be dismissed at once, for the slow fall of pressure occurs long after all the sodium chloride has diffused out of the osmometer.

It may be remarked here that in the foregoing experiments the contents of the osmometer acquire a muddy-brown appearance after about forty-eight hours' dialysis. This appears to be due to the presence of a very fine colloidal suspension. This change in the appearance of the osmometer contents sets in more rapidly at higher temperatures. Moreover, it is found that the muddy-brown solution is unaffected by a small quantity of sodium chloride, whereas a trace of sodium hydroxide suffices to reconvert it into the original bright red solution. We may dismiss, therefore, the hypothesis of Biltz and von Vegesack, and conclude that a slow hydrolysis, accompanied by the diffusion out of sodium hydroxide, and the precipitation in fine, semi-colloidal suspension of some very insoluble substance (perhaps a mixture, or "adsorption-compound," of Congo-red acid, or the acid salt, with the original Congo-red), is occurring. This would give a satisfactory explanation of the gradual fall in osmotic pressure. Were this the case, we should expect to be able to prevent this "membrane-hydrolysis," and so obtain constant osmotic pressures by employing instead of pure water a dilute solution of sodium hydroxide as external liquid. Experiment confirms this conclusion, for the employment of a $N/800$-sodium hydroxide solution suffices entirely to prevent the "precipitation" of an 0·5 per cent. solution of Congo-red at 25°, and enables a perfectly definite and constant osmotic pressure to be obtained. These results enable us also to understand why Bayliss found that carbon dioxide exerted a marked action in lowering the osmotic pressure of Congo-red solutions; for the carbonic acid in the external water will combine with the alkali

that diffuses out, and so hasten and increase the hydrolysis and precipitation in the osmometer. The following experiment will serve to confirm this conclusion. Two similar osmometers were filled with the same 0·5 per cent. solution of Grübler's Congo-red. In the case of one osmometer, entrance of carbon dioxide was prevented as described previously. The other osmometer was simply suspended in an open beaker containing a volume of ordinary distilled water equal to the volume of water, free from carbon dioxide, in the protected outer jar of the first osmometer. The osmotic pressure fell, in one case, from 82·5 mm. to 69·5 mm. in seventeen days, whilst in the other case (unprotected osmometer) it fell in the same time from 85·5 to 53·5 mm.

The gradual hydrolysis of Congo-red on dialysis with continued change of the outer water was conclusively proved as follows: 100 c.c. of a 0·5 per cent. solution of Merck's Congo-red were placed in a parchment dialysing tube, which was suspended in a beaker containing a litre of distilled water. This outer water was changed every day. The original Congo-red (Merck's) was found to contain 16·47 per cent. of sodium, showing the presence of a fairly large amount of foreign electrolytes (sodium chloride and sulphate). After four days' dialysis a portion of the solution was evaporated to dryness, and the sodium content of the dry residue determined. This was found to be 6·5 per cent. (theoretical value for Congo-red, 6·6 per cent.). After three weeks' dialysis the sodium content of the dried residue obtained on evaporation was found to be 6·0 per cent., thus indicating a loss of total sodium due to hydrolysis and diffusion out of sodium hydroxide. In order to obtain a more marked difference, a diluted solution of the muddy-brown liquid obtained after three weeks' dialysis was subjected to further dialysis with daily renewal of the external water. After seven weeks' dialysis the muddy solution in the dialyser had assumed a violet hue, and the dried residue was now found to contain only 1·6 per cent. of sodium. A portion of this solution, still further diluted, on boiling in a glass beaker for some time became clear and bright red, being converted into a solution of the normal Congo-red salt by the alkali taken up from the glass. The above dialysed solution (total concentration about 0·15 gram per 100 c.c., sodium content of dry residue = 1·6 per cent.) gave in an osmometer an osmotic pressure of 40 mm. of water, that is, about 3 mm. of mercury, the measurement being made by substituting a vertical glass tube of narrow bore for the mercury manometer. This result appears to indicate that the first product of the hydrolysis of Congo-red must be mainly a "colloidal" suspension of the sodium hydrogen salt, since, if the free acid were in suspen-

sion, the solution which still contains 1·6 per cent. of sodium in its solid residue ought to have shown a much higher osmotic pressure than that observed.

A similar experiment with Kahlbaum's benzopurpurine-4B yielded the following results:

Initial sodium content of Kahlbaum's preparation	=	22·45 per cent. Na.
Sodium content of dried residue after six days' dialysis	=	6·0 per cent. Na.
Sodium content of dried residue after five weeks' dialysis	=	3·3 per cent. Na.*
Theoretical value for benzopurpurine	=	6·3 per cent. Na.

* The solution in the osmometer after five weeks' dialysis contained approximately 1 gram per 100 c.c.

These results show that benzopurpurine suffers a much more rapid membrane-hydrolysis than Congo-red. This accounts for the fact that Biltz and von Vegesack found a solution of benzopurpurine (of initial concentration 1 per cent.) after three weeks' dialysis to show only a small osmotic pressure. The following experiment confirms this conclusion. A solution of benzopurpurine gave an osmotic pressure of 67·5 mm. of mercury, which fell to 6 mm. in fourteen days (final concentration about 0·25 per cent.), whilst with a Congo-red solution of final concentration 0·17 per cent. the pressure fell from 48 mm. to 34 mm. in nineteen days.

Second Series of Osmotic Pressure Measurements.

In the previous experiments the maximum pressures observed corresponded with solutions which had suffered some degree of hydrolysis, and were in consequence muddy-brown in appearance. In order to see whether this hydrolysis had sensibly vitiated the results, a series of experiments with solutions of the same initial concentrations of Grübler's Congo-red was carried out as follows. After the preliminary dialysis in the osmometer against pure water to remove the sodium chloride, a dilute solution of sodium hydroxide* was used as external liquid in order to throw back the hydrolysis. This solution was then replaced by a more dilute solution of alkali, and so on, pure water being finally employed. In this way one may hope to obtain the maximum osmotic pressure against pure water without sensible disturbance, due either to hydrolysis or to presence of foreign electrolytes. The results are shown in the following table:

* Prepared from metal and pure water free from carbonic acid.

Room temperature 17°.

	Osmom. I.	Osmom. II.	Osmom. III.
Initial concentration (gram per 100 c.c.) (Congo-red + NaCl)	0·5	0·75	1·00
	mm. Hg.	mm. Hg.	mm. Hg
Max. reading after removal of NaCl	82·0	132·0	166·5
Reading after 24 hours with *N*/500-NaOH	52·0	90·0	132·0
,, ,, ,, *N*/1000-NaOH	57·0	104·0	143·0
,, ,, ,, *N*/2000-NaOH	68·0	117·0	156·0
,, ,, ,, *N*/4000-NaOH	79·0	128·0	165·0
,, ,, ,, *N*/8000-NaOH	81·0	131·0	167·0
,, ,, ,, *N*/16,000-NaOH ...	84·0	137·0	169·0
,, ,, ,, pure water.........	86·0	137·5	171·0
Correction for difference of levels	+ 3·0	+ 7·5	+ 0·7
Final osmotic pressure	89·0	145·0	171·7
Final concentration (gram per 100 c.c.)	0·357	0·564	0·700
"Calculated value" of osmotic pressure	92·7	146·4	179·0
Observed as percentage of calculated value	96·0%	99·0%	96·5%

These results satisfactorily substantiate those previously obtained, and show that at these concentrations and temperatures the osmotic pressure of a pure non-hydrolysed Congo-red solution approaches closely to that calculated for single undissociated molecules.

Third Series of Osmotic Pressure Measurements.

In these experiments, which were carried out according to Bayliss' method for the sake of comparison, the osmometer contained initially a solution (that is, colloidal solution) of pure Congo-red acid (prepared by dialysis of a mixture of Congo-red and hydrochloric acid). In the first experiment *N*/175-sodium hydroxide solution was employed initially as external liquid, in order to convert the Congo-red acid in the osmometer into the Congo-red (sodium) salt. After ten days this was replaced by *N*/1000-sodium hydroxide, which solution was replaced by *N*/2000-sodium hydroxide after twenty-four hours. The alkali solution was then regularly replaced by a more dilute one every twenty-four hours, and finally by pure water. The volume of outer liquid was 1 litre, as in the previous experiments, the temperature 17°. The following table shows the result of one experiment:

Concentration of alkali.	Difference of mercury levels.	Concentration of alkali.	Difference of mercury levels.
N/175	31·0 mm.	*N*/8000	116·5 mm.
N/1000	76·0 ,,	*N*/16,000	122·0 ,,
N/2000	98·0 ,,	*N*/32,000	121·5 ,,
N/4000	113·0 ,,	Water	121·0 ,,

The correction for difference of water and mercury levels was −2 mm., so that the maximum osmotic pressure observed was

120 mm. The final concentration of Congo-red being 0·491 gram per 100 c.c., the calculated value = 124 mm. Hence, observed value = 97 per cent. of calculated value.

Two other similar experiments gave the following final results:

Final conc. of Congo-red.	Observed pressure.	Calculated value.	Percentage.
0·423 gram/100 c.c.	106·0 mm. Hg.	109·5 mm.	97·0
0·346 ,,	88·7 ,,	90·0 ,,	98·5

These results show a good general agreement with those obtained by the other method.

Fourth Series of Osmotic Pressure Measurements.

These experiments were made with much more concentrated solutions of Congo-red. No alkali was used in the outside water. The latter was changed daily until no more sodium chloride diffused out, this requiring four to five days in the relatively more dilute solutions, and about eight days in the more concentrated solutions. As in the first series of measurements, the pressure rose to a maximum, and then slowly decreased, this maximum being reached after the sodium chloride was all (or practically all) removed. The final results are shown in the following table:

Final concentration.	Max. pressure observed.	Calculated value.	Percentage.
1·276 per cent.	310 mm.	331·8 mm.	93·4
2·617 ,,	603 ,,	676·0 ,,	89·0
5·016 ,,	1139 ,,	1304·0 ,,	87·3
6·033 ,,	1363 ,,	1567·0 ,,	86·9

In the last experiment in this series the form of manometer described by Adie (Trans., 1891, **59**, 234) was employed. These results point perhaps to an increasing "aggregation" of the Congo-red in the stronger solutions, the osmotic pressure per molecule of Congo-red decreasing with increase of concentration.

Behaviour of Sodium Chloride and Sodium Hydroxide alone in the Osmometer.

A detailed examination of this behaviour was made, the results of which need only be briefly referred to. With the sodium chloride solutions ($5N$, $N/10$, $N/100$, $N/1000$) the pressure developed initially falls rapidly at first, afterwards very slowly. This is due to the fact that even when the salt has practically all diffused out, the hydrostatic pressure so established only falls slowly, owing to the slow rate at which water flows through the parchment diaphragm under small differences of pressure. A rapid rise, followed by a rapid fall of pressure, was observed at each change of the external water. This effect is very different from the otherwise somewhat similar one observed in the case of Congo-red solutions

which are being freed from sodium chloride by dialysis. In the present case the rapid rise and succeeding rapid fall of pressure are undoubtedly due to the temporary osmotic pressure caused by the salt still present in the osmometer. In the case of the Congo-red solutions referred to, the rise of pressure on change of the external water is followed by a slow fall of pressure, the latter being due, as shown above, to the progressive membrane-hydrolysis; whilst the rise is due to the removal of the counter-pressure caused by the greater concentration of the salt in the external water.

A concentrated solution of sodium hydroxide appears to pass through the membrane very rapidly, whilst weak solutions do so very much more slowly. The conclusion of Roaf (*loc. cit.*) that diffusible electrolytes do not show any temporary osmotic pressure effects with parchment membranes is therefore incorrect. The following tables will give some idea of the nature of the results observable with the osmometers used in this work.

5*N*-Sodium chloride.

Time from filling.	Pressure.
$7\frac{3}{4}$ hours	169·0 mm.
*48 ,,	42·0 ,,
53 ,,	54·5 ,,
* 4 days	33·5 ,,
4 ,, 8 hours	35·0 ,,
5 ,,	27·5 ,,
* 6 ,,	20·0 ,,
6 ,, 8 hours	20·0 ,,
7 ,,	18·0 ,,
10 ,,	11·0 ,,

N/10-Sodium chloride.

Time from filling.	Pressure.
$18\frac{1}{2}$ hours	56·7 mm.
68 ,,	24·0 ,,
*116 ,,	17·0 ,,
140 ,,	26·0 ,,
*188 ,,	20·0 ,,
194 ,,	19·5 ,,

N/2-Sodium hydroxide.

0 hour	25·5 mm.
*18 hours	2·5 ,,
49 ,,	36·4 ,,
*90 ,,	29·0 ,,
95 ,,	35·4 ,,
*118 ,,	26·5 ,,
124 ,,	26·0 ,,
160 ,,	17·0 ,,

N/1000-Sodium hydroxide.

0 hours	23·0 mm.
3 ,,	36·0 ,,
*22 ,,	24·0 ,,
28 ,,	21·0 ,,
70 ,,	14·5 ,,
119 ,,	9·9 ,,

* Indicates change of outside liquid.

Electrical Conductivity of Congo-red Solutions.

In order to prepare Congo-red solutions for measurements of electrical conductivity, it was necessary to free them as far as possible from sodium chloride by dialysis, and at the same time to avoid any appreciable hydrolysis. For this purpose the hot saturated solution of Congo-red was placed in an osmometer vessel, the side-tube of which was closed by a rubber-tube and screw-clip. The osmometer vessel was then immersed in distilled water, free from carbon dioxide, which was changed daily for nineteen days.

By thus dialysing strong solutions at room temperature, and preventing dilution of the solutions during dialysis caused by osmotic flowing in of water, any appreciable hydrolysis was prevented, as it was found that hydrolysis increased the more dilute the solutions were. The contents of the osmometer at the end of the dialysis were diluted with "conductivity" water until the solid which had separated in the osmometer on cooling was all dissolved. Small portions of this solution, when diluted further with water, showed a clear red colour, indicating the absence of any appreciable hydrolysis.

The following table shows the results of the first series of measurements (temp. 25°). The more dilute solutions were obtained by diluting the dialysed solution with conductivity water.

Concentration of Congo-red.			
Grams/100 c.c.	Mols./litre.	Specific conductivity.	Molar conductivity.
2·667	1/26·1	$4·161 \times 10^{-3}$	108·5
1·333	1/52·2	$2·284 \times 10^{-3}$	119·2
0·667	1/104·4	$1·249 \times 10^{-3}$	130·4
0·333	1/208·8	$0·700 \times 10^{-3}$	146·2
0·1667	1/417·6	$0·390 \times 10^{-3}$	163·1
0·0833	1/835·2	$0·210 \times 10^{-3}$	175·7
0·0417	1/1670·4	$0·110 \times 10^{-3}$	183·5
	N/50-NaCl	$2·328 \times 10^{-3}$	116·4

For comparison are given the specific and molar conductivities of a *N*/50-sodium chloride solution at the same temperature. A portion of the strongest of the above dialysed solutions of Congo-red was evaporated to dryness, and the chlorine content of the dried residue determined. The analysis showed that the solution was not quite free from sodium chloride, containing 0·005 gram per 100 c.c. (that is, *N*/1170 with respect to sodium chloride).

A second solution of Congo-red was therefore dialysed in a similar manner for fourteen days, but in order to hasten the removal of the sodium chloride, a small air-space was left in the osmometer vessel, thus permitting the contents of the latter to be mixed by shaking. In this case the solution of Congo-red so obtained was found to be practically free from sodium chloride. Conductivity measurements with solutions prepared from this solution by dilution with conductivity water gave the following results (25°):

Concentration of Congo-red.			
Grams/100 c.c.	Mols./litre.	Specific conductivity.	Molar conductivity.
2·485	1/28	$3·664 \times 10^{-3}$	102·6
1·2425	1/56	$2·046 \times 10^{-3}$	114·6
0·6212	1/112	$1·125 \times 10^{-3}$	126·0
0·3106	1/224	$0·626 \times 10^{-3}$	140·2
0·1553	1/448	$0·352 \times 10^{-3}$	157·7
0·0776	1/896	$0·189 \times 10^{-3}$	169·3
0·0388	1/1792	$0·102 \times 10^{-3}$	182·8
	N/50-NaCl	$2·328 \times 10^{-3}$	116·4

As a further check, two measurements of osmotic pressure were made at room temperature (17°) with the dialysed solution used in the above conductivity measurements. The results may be briefly stated as follows:

Experiment 1 :—Final concentration of solution	=	0·572 gram per 100 c.c.
Maximum pressure (reached in 4 days)	=	140·0 mm. Hg
Calculated value	=	148·7 ,, ,,
Observed value as percentage of calculated value	=	94
Experiment 2 :—Final concentration of solution	=	0·257 gram per 100 c.c.
Maximum pressure (reached in 3 days)	=	62·5 mm. Hg.
Calculated value	=	66·7 ,, ,,
Observed value as percentage of calculated value	=	94

The conductivity-measurements show that Congo-red in aqueous solution behaves as a highly dissociated salt, although the observed value of the osmotic pressure indicates apparently no ionisation. At first sight one would be inclined to explain this somewhat anomalous result by the assumption of simultaneous "aggregation" and ionisation of the aggregated complex.

Consider, for example, a solution containing 1 gram of Congo-red in 100 c.c. The foregoing measurements show that at 17° the observed osmotic pressure of such a solution is somewhat less than 260 mm. (the value calculated for simple undissociated molecules). Suppose now that the solution contained only undissociated aggregates of the formula $(Na_2R)_{10}$. This would lead to an osmotic pressure of only 26 mm. for the above-mentioned solution. If, however, we were to assume a complete "first stage" ionisation of these complexes according to the equation:

$$(Na_2R)_{10} = 10Na^{\cdot} + (NaR)_{10}^{10-},$$

the osmotic pressure would be 11×26, or 286 mm.

In the same way the assumption of aggregates of the formula $(Na_2R)_{20}$ ionising in a similar manner would lead to an osmotic pressure of 273 mm. The assumption of the existence of such aggregates ionising (partially) in the manner indicated would therefore suffice to account for the osmotic pressures observed, and might perhaps serve to explain the non-diffusibility of Congo-red through parchment paper; but it is difficult to reconcile such an assumption with the high values obtained for the molar conductivities. Consider, for example, the 1/112-molar solution, the molar conductivity (referred to the formula Na_2R) of which at 25° is 126. The observed osmotic pressure of this solution indicates a van't Hoff factor (referred to the formula Na_2R) of practically unity. Let us suppose for a moment that this solution contained complexes of the (average) formula $(Na_2R)_n$, very largely dissociated as indicated by the equation:

$$(Na_2R)_n = nNa^{\cdot} + (NaR)_n^{n-}.$$

Then the molar conductivity referred to Na_2R would be approxi-

mately equal to the conductivity of 1 gram-molecule Na$^{\bullet}$-ion plus $1/n$th the conductivity of 1 gram-molecule $(NaR)_n^{n-}$-ion. Now the latter term cannot exceed the conductivity of 1 gram-molecule $(NaR)^-$-ion, which we may put at about 30—40 at 25°; so that the molar conductivity of the solution cannot certainly exceed at 25° 50 + 40, that is, 90, whilst the observed value is 126. If therefore the observed conductivities correspond with solutions practically free from sodium chloride and not to any appreciable extent hydrolysed, it does not seem possible to reconcile them with any such explanation of the osmotic pressure results as that suggested above. On the other hand, the assumption that we are dealing with a simple salt Na_2R, dissociating into Na$^{\bullet}$-ions and R''-ions, although perhaps reconcilable with the measurements of conductivity, leads to degrees of dissociation and total molecular concentrations which are not in harmony with the observed values of the osmotic pressure. It must not be forgotten in this connexion that the value of the osmotic pressure (if it correspond with a true state of osmotic equilibrium) can be thermodynamically related to the vapour-pressure of the solution, which latter is a function of the total molecular concentration of the solution.

The explanation of this apparent contradiction probably lies in the fact that we are not dealing here with an ordinary case of osmotic equilibrium. The dissociated sodium ions can themselves rapidly pass through the parchment membrane, and are only prevented from doing so by the potential difference set up across the membrane.* True equilibrium can only be attained, as shown in the present paper, when a certain concentration of Na$^{\bullet}$- and $(OH)'$-ions is produced on the other side of the membrane. Under these conditions it is natural to expect that the Na$^{\bullet}$-ions do not contribute in the ordinary way to the osmotic pressure.

The Lowering of the Osmotic Pressure of Congo-red Solutions caused by Solutions of Sodium Chloride and Sodium Hydroxide.

The experiments with pure sodium hydroxide (prepared from metal and water free from carbon dioxide) will first be described. In these experiments it was found that in presence of a definite concentration of sodium hydroxide, provided this concentration was not below a certain critical value, an absolutely constant osmotic pressure was obtained. Evidently in these cases the alkali concentration was sufficient to arrest the membrane-hydrolysis.†

* These questions are fully dealt with in another paper.

† It will be shown in another paper that this experimental result is in full accord with the theory of the action of membranes in presence of electrolytes possessing a non-dialysing ion.

Below a certain concentration of alkali, the critical value being about *N*/1200-sodium hydroxide in the case of a 0·4 per cent. Congo-red solution, the pressure gradually decreased, and the previously clear red solution in the osmometer became muddy, showing that hydrolysis was occurring.

The procedure in the first experiment with sodium hydroxide was as follows. The osmometer was filled with a "solution" of Congo-red acid of concentration approximately the same as that used in the third series of experiments on osmotic pressure. This was converted completely into Congo-red salt by means of an *N*/90-solution of pure sodium hydroxide put outside the osmometer (all entrance of carbon dioxide was, of course, prevented as described previously), the volume of this solution being 1 litre. When the conversion was complete, the alkali solution was replaced by a litre of *N*/100-sodium hydroxide solution, when a constant pressure was attained after two to three days. The concentration of the alkali solution was then reduced to *N*/200, the pressure thereupon rising, and finally becoming quite constant after a few days. The alkali concentration was successively reduced in the way described, until finally pure water was used, which was changed from time to time until the maximum pressure was attained. The results of an experiment at 25° are shown below:

Concentration of alkali.	Osmotic pressure.
N/100	37·0 mm. Hg
N/200	57·7 ,, ,,
N/400	76·3 ,, ,,
N/800	96·0 ,, ,,
N/1200	104·6 ,, ,,
Pure water	114·5 ,, ,, (max. pressure).

In this experiment the final concentration of the Congo-red was 0·395 gram per 100 c.c., for which the calculated value of the osmotic pressure at 25° is 105·5 mm. The observed value in this case exceeds the "calculated value" by about 8 per cent. It is possible that this excess may be partly due to a little alkali still present inside the osmometer, as the maximum pressure was attained about six hours after the *N*/1200-solution had been replaced by pure water.

A second experiment was made at 25° under similar conditions, but after a constant pressure was obtained with *N*/800-sodium hydroxide solution, some sodium chloride was added to the outside liquid so as to make it *N*/800-sodium hydroxide + *N*/500-sodium chloride. The pressure decreased from the value obtained with *N*/800-sodium hydroxide alone, and again became constant. Constant pressures were similarly obtained with *N*/1600-sodium hydroxide + *N*/1000-sodium chloride, and with *N*/3200-sodium

hydroxide + $N/2000$-sodium chloride. After this the concentration of the mixed solution outside the osmometer was decreased daily until it reached the value $N/25,600$-sodium hydroxide + $N/16,000$-sodium chloride, when pure water, free from carbon dioxide, was substituted for it, the (final) concentration of the Congo-red solution in the osmometer being determined when the maximum pressure had been obtained and all sodium hydroxide and sodium chloride had been removed. The results of this second experiment are shown in the accompanying table (temperature 25°).

Concentration.	Osmotic pressure. mm. Hg.	Concentration.	Osmotic pressure. mm. Hg.
$N/100$-NaOH	33·0	$N/800$-NaOH + $N/500$-NaCl	61·0
$N/200$-NaOH	53·0	$N/1600$-NaOH + $N/1000$NaCl	79·0
$N/400$-NaOH	73·0	$N/3200$-NaOH + $N/2000$-NaCl	91·0
$N/800$-NaOH	93·0	Pure water (max. pressure)	107·3

In this experiment the concentration of the Congo-red solution was 0·383 gram per 100 c.c., for which the calculated value of the osmotic pressure at 25° is 102 mm. The observed (maximum) value is therefore about 5 per cent. higher than that calculated for simple undissociated molecules.

It may be remarked that a constant osmotic pressure (that is, absence of membrane-hydrolysis) is obtained with $N/3200$-sodium hydroxide + $N/2000$-sodium chloride, although hydrolysis occurs in presence of $N/1600$-sodium hydroxide alone, which shows that sodium chloride assists the sodium hydroxide in preventing hydrolysis, in spite of the fact (as will be shown presently) that even a fairly strong solution of sodium chloride alone cannot prevent hydrolysis occurring. It may also be remarked that the lowering effect of a mixture of sodium chloride and sodium hydroxide appears to be about the same as that of an equimolecular solution of pure sodium hydroxide. Thus $N/800$-sodium hydroxide + $N/500$-sodium chloride, which corresponds with a pressure of 61 mm., is approximately equimolecular with $N/300$-sodium hydroxide, for which the pressure has very nearly the same value, as may be seen by interpolation from the data given above.

The effect of sodium hydroxide on a more concentrated solution of Congo-red was next investigated. In this experiment the osmometer was filled with a strong solution of Grübler's Congo-red, as used in the fourth series of osmotic pressure measurements. A litre of distilled water, free from carbon dioxide, was placed outside the osmometer, and changed every day for fourteen days, when all the sodium chloride was removed and a maximum pressure of 722 mm. Hg developed. Up to this point the experiment was carried out at room temperature (17°). The pure water was now

replaced by a litre of $N/25$-sodium hydroxide, and the apparatus suspended in a thermostat at 25°. The pressure quickly dropped, becoming constant at 261 mm. in three days. As in the previous experiments, the constant pressures corresponding with more dilute solutions of sodium hydroxide were determined, and finally the alkali was replaced by pure water, which was changed daily until the maximum pressure was attained. The results are shown in the following table:

Concentration of sodium hydroxide.	Pressure.
$N/25$	261·0 mm.
$N/50$	405·0 ,,
$N/100$	551·0 ,,
$N/200$	636·0 ,,
$N/400$	687·0 ,,
Pure water (max. pressure)	763·6 ,,

The final concentration of the Congo-red was 3·10 grams per 100 c.c., for which the calculated value of the osmotic pressure at 25° is 828 mm., the observed value at 25° being thus 92 per cent. of the calculated value. The calculated value at 17° is 806 mm., the observed value (722 mm.) being in this case 89·6 per cent. of the calculated value. The osmotic pressure per molecule of the Congo-red solution appears therefore to increase more rapidly with increase of temperature than would correspond with the simple gas law. The effect of sodium chloride solutions alone on the osmotic pressure of Congo-red was next investigated. It was found, for example, that a normal solution of sodium chloride placed outside the osmometer was sufficient to reduce the osmotic pressure of a saturated solution of Grübler's Congo-red to zero. Under similar conditions a 0·5 per cent. solution of Grübler's Congo-red showed zero pressure, some of the Congo-red salt being precipitated in the osmometer. Another portion of this 0·5 per cent. solution contained in an osmometer immersed in $N/25$-sodium chloride solution showed a pressure of only 60 mm. of water (about 4·4 mm. Hg), no precipitation occurring in this case.

It was not possible to carry out exact measurements with sodium chloride as in the case of sodium hydroxide, for the pressures always fell slowly after attaining a maximum, owing to progressive hydrolysis.

The following is an example of many similar experiments. An osmometer was filled with a 2·5 per cent. solution of Grübler's Congo-red, and immersed in a litre of pure water, free from carbon dioxide, at room temperature (17°). The greater portion of the sodium chloride was removed by dialysis, which was continued for two days, with three changes of water. The pressure at this point having risen to 203 mm., the outside water was replaced by a

N/25-sodium chloride solution, the pressure immediately falling and becoming fairly steady at 82 mm. in three to four days. The concentration of the outside sodium chloride solution was then successively reduced, and the approximately steady values of the pressure noted. Finally, pure water was used, and changed daily until all salt was dialysed out and the maximum pressure obtained. The results are given below (temperature 17°).

Concentration of sodium chloride.	Pressure.
N/25	82 mm.
N/50	131 ,,
N/100	191 ,,
N/200	259 ,,
Pure water (max. pressure)	365 ,,

This solution contained 1·713 grams of Congo-red per 100 c.c., for which the calculated value of the pressure at 17° is 446 mm. The observed maximum pressure is only 82 per cent. of this, which is to be accounted for by hydrolysis occurring in the osmometer, the dialysis having lasted thirty-one days in all.

Cause of the Lowering of Pressure produced by Sodium Chloride and Sodium Hydroxide.

If the remarkable effects produced by sodium chloride and sodium hydroxide on the osmotic pressure of a Congo-red solution were due solely, as Bayliss supposes, to an increased aggregation of the Congo-red, we might expect this to show itself in a greatly reduced conductivity. Experiment shows, however, that on mixing a solution of pure Congo-red with enough sodium chloride solution to effect an enormous lowering in the measured osmotic pressure, the conductivity of the mixed solution only shows the usual small deviation from the additive law to be expected in a mixture of two strong electrolytes which slightly influence each other's dissociation. The following data illustrate this, the values given being the conductances (not the specific conductivities), as measured in a certain conductivity cell at 25° (in reciprocal ohms).

Concentration of Congo-red solution = 2·485 per cent.

10 c.c. of Congo-red solution + 10 c.c. of conductivity water	$2{\cdot}651 \times 10^{-2}$
10 c.c. of *N*/50-sodium chloride + 10 c.c. of conductivity water......	$1{\cdot}565 \times 10^{-2}$
10 c.c. of Congo-red solution + 10 c.c. of *N*/50-sodium chloride......	$3{\cdot}940 \times 10^{-2}$

It will be seen that the last value is only slightly less than the sum of the two others. From the table given above it will also be seen that a *N*/50-sodium chloride solution lowers the osmotic pressure of a Congo-red solution (containing 1·7 grams of Congo-red per 100 c.c.) from 365 mm. to 131 mm.

Before discussing another possible explanation of the effects produced by sodium chloride and sodium hydroxide on the osmotic

pressure, an account will be given of experiments which have revealed a new and hitherto quite unsuspected phenomenon. It will be shown that when Congo-red is present on one side of a parchment diaphragm, sodium chloride (that is, total Cl'-ion) does not distribute itself in equal concentration on both sides, although the membrane of parchment paper is perfectly permeable to both $Na^{\cdot}$ and Cl'.

In the first experiment, 5 grams of Merck's Congo-red dissolved in 200 c.c. of distilled water, free from carbon dioxide, were placed inside a parchment dialysing tube suspended in a large beaker containing a litre of pure distilled water. By means of three changes of water the greater portion of the admixed salts was removed, the dialysis being continued for twenty-four hours. Then the outer water was replaced by a litre of $N/10$-sodium chloride solution. After thirteen days the chlorine content of the inside and outside liquids was determined. This was done by withdrawing 50 c.c. of each by means of a pipette, evaporating to dryness, heating the residues over a Bunsen flame for about a quarter of an hour (by which procedure the Congo-red from the inner liquid was charred, the residue from the outer liquid being subjected to the same process so as to have similar conditions), extracting with hot water, and estimating as silver chloride by precipitation in the usual way. The results were as follows:

Outer liquid: 5·106 grams of sodium chloride per litre.
Inner liquid: 4·478 ,, ,, ,, ,, ,,

The concentration of the Congo-red in the inner solution was determined, and found to be 1·074 per cent. At the same time the conductances of a given cell (at 25°) filled with each of the two solutions were determined, with the following results:

Liquid used.	Conductance of cell (in mhos).
Inner	$12·99 \times 10^{-2}$
Outer	$12·50 \times 10^{-2}$

The foregoing experiment shows that after thirteen days' dialysis the concentration of the sodium chloride in the outer solution is undoubtedly greater than that in the inner solution containing the Congo-red. In order to obviate the natural objection that in the above experiment the sodium chloride might have been still diffusing into the inner solution, two further experiments were made, in which the concentration of the sodium chloride was initially higher in the inner solution (containing the Congo-red). In the first experiment, a mixture of approximately 2·8 grams of pure Congo-red and 7·2 grams of sodium chloride dissolved in 200 c.c. of conductivity water was placed inside the dialyser and a litre of pure water outside. After six days' dialysis the inner

liquid contained 5·136 grams of sodium chloride per litre, and the outer liquid 5·728 grams. The concentration of Congo-red in the inner liquid was 0·917 gram per 100 c.c.

In the next experiment the inner solution consisted initially of about 2·1 grams of pure Congo-red and 3·9 grams of sodium chloride, dissolved in 200 c.c. of pure water, the outer liquid being, as before, a litre of pure water. After five days' dialysis the inner liquid contained 2·53 grams of sodium chloride per litre, and the outer liquid 3·03 grams. The concentration of Congo-red in the inner liquid was 0·875 gram per 100 c.c.

These results show that we are dealing with a reversible equilibrium, and that the equilibrium state corresponds with a greater concentration of sodium chloride on the opposite side of the membrane to the Congo-red. Now this unequal distribution will clearly set up, in the osmotic pressure experiments, a counter osmotic pressure, which will make the observed osmotic pressure lower than that corresponding with the Congo-red.

The following calculation will serve to indicate the amount of this counter pressure. Consider the first of the three experiments given above. The osmotic pressure (at 0°) of the outer solution of sodium chloride will be $22{\cdot}4 \times 760 \times \frac{5{\cdot}106}{58{\cdot}5} \times i_1$ mm. Hg, where i_1 = van't Hoff's factor for a solution of this concentration. The osmotic pressure due to the sodium chloride concentration in the inner solution will be similarly $22{\cdot}4 \times 760 \times \frac{4{\cdot}478}{58{\cdot}5} \times i_2$. Putting $i_1 = i_2 = 1{\cdot}85$, we get for the counter osmotic pressure at 17° (in mm. Hg):

$$22{\cdot}4 \times 760 \times \frac{290}{273} \times \frac{0{\cdot}628}{58{\cdot}5} \times 1{\cdot}85,$$

or 359 mm. Now the osmotic pressure at 17° of the Congo-red solution present in this experiment (containing 1·074 per cent. of Congo-red) would, according to the data given previously, amount to about 290 mm. Hence the approximately $N/12$-solution of sodium chloride of this experiment would more than suffice to annul the osmotic pressure of the 1·074 per cent. Congo-red solution.

These considerations show that the unequal concentrations of an electrolyte (such as sodium chloride) with a common ion, which exist at equilibrium on either side of the membrane in presence of Congo-red on one side only, are sufficient to explain the apparent lowering effect of these electrolytes on the osmotic pressure of a solution of Congo-red. The results obtained by Bayliss with Congo-red and by Biltz and Vegesack with benzopurpurine are now intelligible, without any special assumptions as to the effect of the

electrolytes on the aggregation of the molecules of the electrolytic colloid. It is, of course, possible that some such aggregation may occur, but the results of the present paper show that the unequal distribution discovered in the present work is a sufficient explanation.

This unequal distribution can be easily shown to be thermodynamically necessary.* Suppose we have on one side of a membrane a solution of the salt NaX, the membrane being supposed permeable to $Na^{\cdot}$, but impermeable to X' and to undissociated NaX. Let now a solution of sodium chloride be put on the other side of the membrane, the latter being supposed permeable to Cl' and sodium chloride. The initial state can be represented as follows:

$Na^{\cdot}$	$Na^{\cdot}$
X'	Cl'
(1)	(2)

$Na^{\cdot}$- and Cl'-ions will now begin to diffuse from (2) to (1). Equilibrium will be attained when the work gained by the isothermal reversible transport of δn gram-mol. Cl'-ion from (2) to (1) is equal to the work required for the isothermal reversible transport of δn gram-mol. $Na^{\cdot}$-ion from (2) to (1), that is:

$$\delta n . RT \log \frac{[Na^{\cdot}]_1}{[Na^{\cdot}]_2} = \delta n . RT \log \frac{[Cl']_2}{[Cl']_1},$$

where the square brackets indicate molar concentrations at equilibrium.

Hence:
$$\frac{[Na^{\cdot}]_1}{[Na^{\cdot}]_2} = \frac{[Cl']_2}{[Cl']_1}.$$

Now since at equilibrium we have in (1) both NaX and sodium chloride, in general $[Na^{\cdot}]_1 > [Cl']_1$. Also from the above $[Cl']_2^2 = [Na^{\cdot}]_1 \times [Cl']_1$. Hence $[Cl']_2 > [Cl']_1$. For highly dissociated solutions we shall therefore find the total "chlorine" concentration in (2) greater than that in (1). This has actually been shown to be the case in the experiments described in this paper.

Since the conclusion of this work a further paper has been published by Biltz and von Vegesack (*Zeitsch. physikal. Chem.*, 1910, **73**, 481), in which, contrary to their previous work, they find that both benzopurpurine and Congo-red exhibit considerable osmotic pressures. From measurements made in presence of other electrolytes they obtain values for the osmotic pressure which lead them to the conclusion that the true value for the molecular weight of Congo-red in aqueous solution is in the neighbourhood of 2000. It may be pointed out, however, that this conclusion is not binding,

* In a paper which is ready for publication, the thermodynamical theory of such 'membrane equilibria" will be more fully considered.

for, as shown in the present paper, the other electrolytes present will be unequally distributed on either side of the membrane, and so give rise to a counter osmotic pressure. The experimentally observed pressure will therefore be lower, and the value calculated for the molecular weight higher, than that which would be obtained if no foreign electrolytes were present.

Summary of Results.

(1) It has been shown that Congo-red gives against pure water an osmotic pressure agreeing approximately with that which would be obtained if it existed in aqueous solution as single undissociated molecules. The values found agree as to order of magnitude with those recorded by Bayliss (*loc. cit.*).

(2) Conductivity measurements show that Congo-red is a highly dissociated electrolyte.

(3) From the results of the conductivity measurements it is concluded that Congo-red exists in aqueous solution very largely as a simple and considerably dissociated salt.

(4) On dialysis, both Congo-red and benzopurpurine-4B undergo a peculiar "membrane-hydrolysis," sodium ions in company with hydroxyl ions diffusing out, and the free acids, acid salts, or some other insoluble phase being gradually aggregated or thrown out of solution inside the dialyser or osmometer. This "membrane-hydrolysis" can be prevented by solutions of alkali hydroxide above a certain definite concentration, the latter varying with the temperature and the concentration of the dye-salt. The gradual fall of osmotic pressure observed with pure water as external liquid is due to the membrane-hydrolysis.

(5) A consideration of the results given under (1) to (4) show that the osmotic pressures observed do not correspond with an ordinary state of osmotic equilibrium, inasmuch as the otherwise diffusible sodium ions are arrested in their diffusion across the membrane by potential differences, and do actually pass slowly through, to a certain extent, in company with hydroxyl ions.

(6) The osmotic pressure of a solution of Congo-red is lowered by sodium hydroxide and sodium chloride, the fall of pressure increasing with the concentration of these electrolytes.

(7) Sodium chloride distributes itself in unequal concentrations on either side of the parchment paper membrane when Congo-red is present on one side. A reversible ionic equilibrium is produced, the concentration of the sodium chloride at equilibrium being higher on the side of the membrane opposite to that in which the Congo-red is present.

(8) This highly important and interesting "membrane-equili-

brium" has been shown to be thermodynamically necessary, and is part of a group of very general and important phenomena.

(9) The counter osmotic pressure caused by the unequal distribution of sodium chloride (or sodium hydroxide) referred to in (7) is probably to a very large extent sufficient to account for the effects described under (6).

(10) Measurements of the osmotic pressures exhibited by an electrolyte with a non-dialysable ion in presence of other electrolytes cannot be used to draw conclusions concerning the molecular state in solution of the former, unless account be taken of the unequal distribution referred to in (7) and (9).

THE MUSPRATT LABORATORY OF PHYSICAL AND
ELECTRO-CHEMISTRY, UNIVERSITY OF LIVERPOOL.

CLXXVIII.—*Synthesis of Polypeptides of α-Amino-*n-*nonoic Acid with Glycine, Alanine, Valine, Leucine, Asparagine, and Aspartic Acid.*

By ARTHUR HOPWOOD and CHARLES WEIZMANN.

As peptides of α-amino-*n*-nonoic acid with glycine and other amino-acids probably occur in the degradation products of the proteins contained in beet root, the leaves of *Pelargonium roseum*, and other plants, the authors have prepared the dipeptides of α-amino-*n*-nonoic acid with glycine, alanine, valine, leucine, asparagine, and aspartic acid, and, in addition, the tripeptide leucyl-α-amino-*n*-nonoylglycine.

EXPERIMENTAL.

The method of synthesis adopted was the same as that which the authors (this vol., p. 571) applied in the synthesis of dipeptides of α-aminolauric acid with glycine and other amino-acids. Briefly, the method consists in condensing α-bromo-*n*-nonoyl chloride with the amino-acids in presence of sodium hydroxide, and then displacing the bromine in the product by an amino-group through the action of ammonia.

*α-Bromo-*n*-nonoyl Chloride*, $C_8H_{16}Br{\cdot}COCl$.

One hundred and forty grams of phosphorus pentachloride are added gradually, with vigorous shaking, to 170 grams of α-bromo-*n*-nonoic acid, and, after the energetic action has subsided, the

mixture is heated on a water-bath for an hour. The product is distilled under diminished pressure, and the fraction boiling at 100—120°/9 mm. is collected. Yield, 150 grams:

0·2570 gave AgCl + AgBr = 0·3341. Cl + Br = 45·28.

$C_9H_{16}OClBr$ requires Cl + Br = 45·17 per cent.

*α-Bromo-*n*-nonoyl chloride* is a colourless liquid, which boils at 108—110°/9 mm., and at 118—125°/15 mm. It has a pungent odour, and is decomposed slowly by water and fairly readily by alkalis.

*α-Bromo-*n*-nonoylglycine*, $C_8H_{16}Br\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$.

Ten grams of α-bromo-*n*-nonoyl chloride (1 mol.) and 50 c.c. of *N*-sodium hydroxide (1·25 mol.) are added gradually and alternately, with frequent shaking, to a solution containing 2·9 grams of glycine (1 mol.) dissolved in 40 c.c. of *N*-sodium hydroxide (1 mol.). The solution is heated on a water-bath until the odour of α-bromo-*n*-nonoyl chloride disappears, then allowed to cool, and dilute hydrochloric acid added in slight excess. A colourless precipitate of impure *α-bromo-*n*-nonoylglycine* separates out, which is kept for several hours, then collected, washed with cold water, and dried in air on a porous plate. Yield, 9·1 grams. On crystallising the product from benzene, a mixture of colourless, rhombic plates and rhombic prisms is obtained, which melts at 115·5—117° to a colourless liquid. The crystals are sparingly soluble in cold, but fairly soluble in hot, water or benzene. They are readily soluble in alcohol, ether, or alkalis:

0·1520 gave 0·0959 AgBr. Br = 26·85.

$C_{11}H_{20}O_3NBr$ requires Br = 27·17 per cent.

*α-Amino-*n*-nonoylglycine*, $NH_2\cdot C_8H_{16}\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$.

Five grams of α-bromo-*n*-nonoylglycine are mixed with excess of concentrated aqueous ammonia, and then heated at 100° for an hour in a pressure flask. The resulting solution is evaporated slowly on a water-bath until the excess of ammonia is removed. In order to remove the ammonium bromide and unchanged α-bromo-*n*-nonoylglycine, the dry residue is boiled with absolute alcohol, and then collected, when 3·5 grams of nearly pure *α-amino-*n*-nonoylglycine* are obtained. For further purification, the dipeptide is dissolved in absolute alcohol containing a little aqueous ammonia, the solution filtered, and the filtrate boiled until the ammonia disappears, when the pure peptide separates out, and is collected, washed with absolute alcohol, and dried in air on a porous plate. It forms a mixture of colourless, monoclinic needles and rhombic

plates, which sinters at 205°, and melts and decomposes at 215—216°:

0·2462 gave 0·5160 CO_2 and 0·2143 H_2O. C=57·15; H=9·74.

0·2937 „ 31·4 c.c. N_2 at 17·6° and 750 mm. N=12·40.

$C_{11}H_{22}O_3N_2$ requires C=57·35; H=9·63; N=12·17 per cent.

The dipeptide is fairly soluble in water, almost insoluble in alcohol or benzene, but readily soluble in ammonia, alkali hydroxides, or mineral acids. When dissolved in dilute sulphuric acid, it gives a white, amorphous precipitate with an aqueous solution of phosphotungstic acid, which, as in the case of the proteins, is soluble in excess of the reagent. In presence of sodium hydroxide, the dipeptide condenses with β-naphthalenesulphonyl chloride, yielding *β-naphthalenesulphonyl-α-amino*-n-*nonoylglycine*, which crystallises from water in colourless, rhombic prisms and rhombic plates, melting sluggishly at 203—206° to a viscid, yellow liquid, which darkens on further heating, and suddenly turns to a mobile, brown liquid at 213—215°.

*α-Bromo*iso*hexoyl-α-amino*-n-*nonoylglycine*,

$CHMe_2\cdot CH_2\cdot CHBr\cdot CO\cdot NH\cdot C_8H_{16}\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$.

One gram of α-amino-*n*-nonoylglycine (1 mol.) dissolved in 5·5 c.c. of *N*-sodium hydroxide (1·25 mol.), when treated with 1·23 grams of α-bromo*iso*hexoyl bromide (1·1 mol.) and 6·5 c.c. of *N*-sodium hydroxide (1·5 mol.) in the same way as previously described for α-bromo-*n*-nonoylglycine, and afterwards acidified with hydrochloric acid, yields 2·0 grams of impure *α-bromo*iso*hexoyl-α-amino*-n-*nonoylglycine*. The product crystallises from benzene or dilute alcohol as a mixture of colourless, prismatic needles and rhombic plates. When crystallised from benzene, the mixture of stereoisomerides melts sluggishly at 88—96°, yielding a colourless liquid, but when crystallised from dilute alcohol the mixture melts at 116—119°. The crystals are sparingly soluble in cold, but moderately so in hot, water. They are sparingly soluble in cold, but readily so in hot, benzene. They are also readily soluble in cold absolute alcohol, ether, ammonia, or alkali hydroxides:

0·1560 gave 0·0730 AgBr. Br=19·92.

$C_{17}H_{31}O_4N_2Br$ requires Br=19·63 per cent.

Leucyl-α-amino-n-*nonoylglycine*,

$CHMe_2\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot C_8H_{16}\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$.

One gram of α-bromo*iso*hexoyl-α-amino-*n*-nonoylglycine, when treated with aqueous ammonia in the same way as described for α-bromo-*n*-nonoylglycine, yields 0·7 gram of *leucyl-α-amino*-n-*nonoyl-*

glycine, which crystallises from alcohol containing a little ammonia as a mixture of colourless, rhombic plates and small needles. When quickly heated, it sinters at 206°, and melts sluggishly with much decomposition at 214—222°. The tripeptide is almost insoluble in water, or dilute or absolute alcohol, but readily dissolves in ammonia, alkali hydroxides, or mineral acids. A white, amorphous precipitate is produced when an aqueous solution of phosphotungstic acid is added to a solution of the tripeptide in dilute sulphuric acid, the precipitate being soluble in excess of the reagent:

0·1006 gave 0·2190 CO_2 and 0·0880 H_2O. C=59·36; H=9·79.
0·1019 „ 11·1 c.c. N_2 at 24·4° and 765·2 mm. N=12·59.
$C_{17}H_{33}O_4N_3$ requires C=59·41; H=9·69; N=12·24 per cent.

*α-Bromo-*n*-nonoylalanine*, C_8H_{16}·Br·CO·NH·CHMe·CO_2H.

3·5 Grams of alanine (1 mol.) dissolved in 40 c.c. of *N*-sodium hydroxide (1 mol.) treated in the same way as previously described for α-bromo-*n*-nonoylglycine with 10 grams of α-bromo-*n*-nonoyl chloride (1 mol.) and 40 c.c. of *N*-sodium hydroxide (1 mol.), and afterwards acidified with dilute hydrochloric acid, yield an oily precipitate of impure α-bromo-*n*-nonoylalanine. On prolonged keeping in an ice-chest, the oil slowly crystallises, and may then be collected, washed with water, and dried. The process may, however, be hastened considerably by extracting the oil with ether, evaporating off the latter at the ordinary temperature, placing the oily residue for a few hours in a vacuum desiccator, and then precipitating the *α-bromo-*n*-nonoylalanine* with light petroleum. Yield, 7·1 grams. The product crystallises from benzene in colourless, rhombic plates, which melt at 135·5—138°, yielding a colourless liquid. The crystals are sparingly soluble in cold, and moderately so in hot, water. They are only sparingly soluble in cold, but readily so in hot, benzene. They are also readily soluble in dilute or absolute alcohol, ether, ammonia, or alkali hydroxides:

0·1276 gave 0·0780 AgBr. Br=26·02.
$C_{12}H_{22}O_3NBr$ requires Br=25·93 per cent.

*α-Amino-*n*-nonoylalanine*, NH_2·C_8H_{16}·CO·NH·CHMe·CO_2H.

Five grams of α-bromo-*n*-nonoylalanine, when treated with aqueous ammonia in the same way as described for α-bromo-*n*-nonoylglycine, yield 3·0 grams of *α-amino-*n*-nonoylalanine*, which crystallises from alcohol in colourless prisms, melting and decomposing at 209—214°. The dipeptide is sparingly soluble in water, moderately so in dilute or absolute alcohol, and readily so in ammonia, alkali hydroxides, or mineral acids. When dissolved in dilute sulphuric acid it gives

a white, amorphous precipitate with an aqueous solution of phosphotungstic acid, which is soluble in excess of the reagent:

0·2033 gave 0·4384 CO_2 and 0·1756 H_2O. C=58·82; H=9·67.
0·1892 „ 18·8 c.c. N_2 at 19° and 769·4 mm. N=11·76.
$C_{12}H_{24}O_3N_2$ requires C=58·96; H=9·90; N=11·48 per cent.

α-Bromo-n-*nonoylvaline*, $C_8H_{16}Br\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CHMe_2$.

4·6 Grams of valine (1 mol.) dissolved in 50 c.c. of *N*-sodium hydroxide (1·25 mol.) treated with 10 grams of α-bromo-*n*-nonoyl chloride (1 mol.) and 50 c.c. of *N*-sodium hydroxide (1·25 mol.) in the same way as previously described for α-bromo-*n*-nonoylglycine, and afterwards acidified with hydrochloric acid, yield 12·0 grams of impure *α-bromo*-n-*nonoylvaline*. The product crystallises from benzene in hexagonal plates, and from dilute alcohol in rhombic plates, which melt at 156—159° to a colourless liquid. The crystals are sparingly soluble in hot, but practically insoluble in cold, water. They are fairly soluble in dilute alcohol, moderately so in hot benzene, and readily so in absolute alcohol, ether, ammonia, or alkalis:

0·1669 gave 0·0936 AgBr. Br=23·87.
$C_{14}H_{26}O_3NBr$ requires Br=23·78 per cent.

α-Amino-n-*nonoylvaline*, $NH_2\cdot C_8H_{16}\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CHMe_2$.

Five grams of α-bromo-*n*-nonoylvaline, when treated with aqueous ammonia in the same way as described for α-bromo-*n*-nonoylglycine, yield 3·5 grams of *α-amino*-n-*nonoylvaline*, which crystallises from alcohol in rhombic plates, sintering at 208°, and melting and decomposing at 223—225°. The dipeptide is sparingly soluble in water or alcohol, but readily so in ammonia, alkali hydroxides, or mineral acids. A white, amorphous precipitate is produced when an aqueous solution of phosphotungstic acid is added to a solution of the dipeptide in dilute sulphuric acid, the precipitate being soluble in excess of the reagent:

0·1205 gave 0·2726 CO_2 and 0·1108 H_2O. C=61·69; H=10·29.
0·2992 „ 26·8 c.c. N_2 at 21·8° and 772 mm. N=10·54.
$C_{14}H_{28}O_3N_2$ requires C=61·70; H=10·36; N=10·29 per cent.

*α-Bromo*iso*valeryl-α-amino*-n-*nonoylvaline*,
$CHMe_2\cdot CHBr\cdot CO\cdot NH\cdot C_8H_{16}\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CHMe_2$.

One gram of α-amino-*n*-nonoylvaline (1 mol.) dissolved in 4·6 c.c. of *N*-sodium hydroxide (1·25 mol.) treated in the same way as previously described for α-bromo-*n*-nonoylglycine with 1·0 gram of α-bromo*iso*valeryl bromide (1·1 mol.) and 5·5 c.c. of *N*-sodium

hydroxide (1·5 mol.), and afterwards acidified with hydrochloric acid, yields 2 grams of impure *α-bromo*iso*valeryl-α-amino*-n-*nonoylvaline.* The product crystallises from benzene in stout, prismatic needles, which melt at 179—181° to a colourless liquid. The crystals are sparingly soluble in hot, and almost insoluble in cold, water. They are only sparingly soluble in cold, but readily so in hot, benzene. They are also readily soluble in absolute alcohol, ether, ammonia, and alkalis:

0·1172 gave 0·0509 AgBr. Br = 18·48.

$C_{19}H_{35}O_4N_2Br$ requires Br = 18·36 per cent.

Valyl-α-amino-n-*nonoylvaline,*

$CHMe_2 \cdot CH(NH_2) \cdot CO \cdot NH \cdot C_8H_{16} \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CHMe_2$.

The conversion of α-bromo*iso*valeryl-α-amino-*n*-nonoylvaline into valyl-α-amino-*n*-nonoylvaline by aqueous ammonia is attended with considerable difficulty. On treating the bromo-compound with concentrated aqueous ammonia, either in the cold for days or at 100° for four hours, practically no change takes place. The stability of α-bromo*iso*valeryl derivatives towards aqueous ammonia appears to be general, as Fischer and Schenkel (*Annalen*, 1907, **354**, 12—20) had similar difficulties with α-bromo*iso*valerylglycine and α-bromo*iso*valerylalanine.

α-Bromo-n-*nonoyl-leucine,* $C_8H_{16}Br \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot CHMe_2$.

Five grams of *r*-leucine (1 mol.) dissolved in 40 c.c. of *N*-sodium hydroxide (1 mol.) when treated in the same way as described for α-bromo-*n*-nonoylglycine with 10 grams of α-bromo-*n*-nonoyl chloride (1 mol.) and 50 c.c. of *N*-sodium hydroxide (1·25 mol.), and afterwards acidified with hydrochloric acid, yield 11 grams of impure *α-bromo*-n-*nonoyl-leucine.* The product crystallises from benzene as a mixture of colourless, rhombic plates and prismatic needles, which melts at 130—132·5° to a colourless liquid. The crystals are sparingly soluble in hot, but almost insoluble in cold, water. They are readily soluble in hot, but sparingly so in cold, benzene. They are also readily soluble in cold absolute alcohol, ether, ammonia, or alkalis:

0·2198 gave 0·1173 AgBr. Br = 22·72.

$C_{15}H_{28}O_3NBr$ requires Br = 22·82 per cent.

α-Amino-n-*nonoyl-leucine,*

$NH_2 \cdot C_8H_{16} \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot CHMe_2$.

Two grams of α-bromo-*n*-nonoyl-leucine, when treated with aqueous ammonia in the same way as described for α-bromo-

n-nonoylglycine, yield 1·5 grams of *α-amino-*n*-nonoyl-leucine*, which crystallises from alcohol in small, prismatic needles, mixed with a few rhombic plates. When heated rapidly, it softens at 234°, and melts and decomposes at 237—238°. The dipeptide is sparingly soluble in water, moderately so in dilute or absolute alcohol, and readily so in ammonia, alkali hydroxides, or mineral acids. When dissolved in dilute sulphuric acid, it yields a white, amorphous precipitate with an aqueous solution of phosphotungstic acid, which is soluble in excess of the reagent:

0·1612 gave 0·3709 CO_2 and 0·1569 H_2O. C = 62·75; H = 10·89.
0·1186 „ 9·8 c.c. N_2 at 22·2° and 773·5 mm. N = 9·73.
$C_{15}H_{30}O_3N_2$ requires C = 62·87; H = 10·56; N = 9·79 per cent.

*α-Bromo-*n*-nonoylasparagine*,
$C_8H_{16}Br\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CO\cdot NH_2$.

5·9 Grams of *l*-asparagine (1 mol.) dissolved in 40 c.c. of *N*-sodium hydroxide (1 mol.) treated in the cold as described for α-bromo-*n*-nonoylglycine with 10 grams of α-bromo-*n*-nonoyl chloride (1 mol.) and 40 c.c. of *N*-sodium hydroxide (1 mol.), and afterwards acidified with dilute hydrochloric acid, yield 14·0 grams of impure *α-bromo-*n*-nonoylasparagine*. The product crystallises from absolute alcohol in rhombic prisms, which melt and decompose at 163—164°. The crystals are moderately soluble in hot, but sparingly so in cold, water. They are only moderately soluble in cold, but readily soluble in hot, dilute or absolute alcohol. They are also readily soluble in cold ammonia or alkalis, but are insoluble in ether or benzene:

0·1486 gave 0·0801 AgBr. Br = 22·94.
$C_{13}H_{23}O_4N_2Br$ requires Br = 22·76 per cent.

*α-Amino-*n*-nonoylasparagine*,
$NH_2\cdot C_8H_{16}\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CO\cdot NH_2$.

One gram of α-bromo-*n*-nonoylasparagine, when treated with aqueous ammonia in the same way as described for α-bromo-*n*-nonoylglycine, yields 0·5 gram of *α-amino-*n*-nonoylasparagine*, which crystallises from absolute alcohol containing a few drops of ammonia in fine needles. It sinters at 236° and melts sluggishly, and decomposes at 251—256°. The dipeptide is only sparingly soluble in water or alcohol, but readily so in ammonia, alkali hydroxides, or mineral acids. When dissolved in dilute sulphuric acid, it yields a white, amorphous precipitate with an aqueous solution of phosphotungstic acid, which is soluble in excess of the reagent:

0·1670 gave 0·3316 CO_2 and 0·1328 H_2O. C=54·16; H=8·90.
0·2544 „ 32·0 c.c. N_2 at 22·7 and 756·9 mm. N=14·46.
$C_{13}H_{25}O_4N_3$ requires C=54·30; H=8·77; N=14·63 per cent.

*α-Bromo-*n*-nonoylaspartic Acid,*
$C_8H_{16}Br{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$.

5·2 Grams of aspartic acid (1 mol.) dissolved in 80 c.c. of *N*-sodium hydroxide (2 mols.) when treated in the same way as described for α-bromo-*n*-nonoylglycine with 10 grams of α-bromo-*n*-nonoyl chloride (1 mol.) and 40 c.c. of *N*-sodium hydroxide (1 mol.), and afterwards acidified with hydrochloric acid, yield an oily precipitate of impure α-bromo-*n*-nonoylaspartic acid. The oil is extracted with ether, the latter evaporated at the ordinary temperature, the residual oil kept for a few hours in a vacuum desiccator, and finally the *α-bromo-*n*-nonoylaspartic acid* is precipitated by light petroleum. The product (7·5 grams) is collected quickly, washed with light petroleum, and crystallised from hot water, separating in prismatic needles, which melt and decompose at 153·5—155·5°. The crystals are moderately soluble in water, readily so in alcohol, ether, ethyl acetate, ammonia, or alkalis, but they are almost insoluble in benzene or light petroleum:

0·1175 gave 0·0630 AgBr. Br=22·81.
$C_{13}H_{22}O_5NBr$ requires Br=22·70 per cent.

*α-Amino-*n*-nonoylaspartic Acid,*
$NH_2{\cdot}C_8H_{16}{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$.

One gram of α-bromo-*n*-nonoylaspartic acid, when treated with aqueous ammonia in the same way as described for α-bromo-*n*-nonoylglycine, yields 0·8 gram of *α-amino-*n*-nonoylaspartic acid*, which crystallises from alcohol in monoclinic needles, melting and decomposing at 231—234°. The dipeptide is very soluble in hot or cold water, but only sparingly so in hot, and almost insoluble in cold, absolute alcohol. It is also readily soluble in ammonia, sodium hydroxide, or mineral acids. When dissolved in very dilute sulphuric acid, it gives a white, amorphous precipitate with an aqueous solution of phosphotungstic acid:

0·1804 gave 0·3573 CO_2 and 0·1356 H_2O. C=54·03; H=8·41.
0·1610 „ 14·0 c.c. N_2 at 21·4° and 758 mm. N=10·06.
$C_{13}H_{24}O_5N_2$ requires C=54·13; H=8·39; N=9·72 per cent.

*Action of Ferments on α-Amino-*n*-nonoylglycine.*

Pancreatic juice activated by kinase, pancreatin (Defresne), trypsine (Merck), or liver extract appears to have no action on

α-amino-*n*-nonoylglycine. Similarly when micro-organisms, like *Bacillus subtilis* or *Bacillus pyocyaneus*, are cultivated on dilute solutions of peptone rendered slightly alkaline with potassium carbonate and saturated with α-amino-*n*-nonoylglycine, there is no change in the dipeptide in twenty-four hours. These negative results contrast remarkably with the action of ferments on the corresponding dipeptide, α-aminolaurylglycine (this vol., p. 576).

In carrying out these biological tests the authors had considerable assistance from Dr. Berthelot, of the Pasteur Institute, Paris.

VICTORIA UNIVERSITY,
MANCHESTER.

CLXXIX.—*Substitution in Aromatic Hydroxy-compounds. Part I. The Action of Nitric Acid on Gallic Acid Trimethyl Ether and Pyrogallolcarboxylic Acid Trimethyl Ether.*

By VICTOR JOHN HARDING.

IT has been known for a long time that many benzenecarboxylic acids containing hydroxy-groups or their ethers when treated with nitric acid give rise to nitro-compounds in which the carboxyl group has been displaced by a nitro-group. Such well-known examples are veratric acid (Tiemann, *Ber.*, 1876, **9**, 939), piperonylic acid (Jobst and Hesse, *Annalen*, 1879, **199**, 70), gallic acid trimethyl ether (Schiffer, *Ber.*, 1892, **25**, 721), and myristicinic acid (Salway, Trans., 1909, **95**, 1165). It has been observed by Oertly and Pictet (*Ber.*, 1910, **43**, 1336) that methyl hydrogen hydrastate when treated with concentrated nitric acid in acetic acid solution gives methyl nitropiperonylate:

also that bromopiperonylic acid under the same conditions yields bromonitromethylenedioxybenzene:

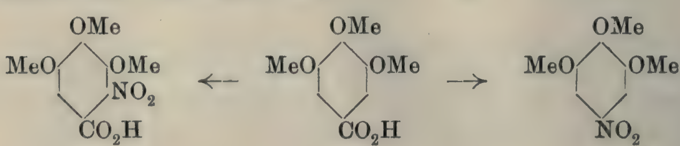
In order to prevent this displacement of the carboxyl group it has so far been found necessary to make use of the alkyl salts when preparing the desired nitro-acid (compare Hamburg, *Monatsh.*, 1898, **19**, 599; Pollak and Feldscharek, *ibid.*, 1908, **29**, 139).

Two years ago Salway (Trans., 1909, **95**, 1155) found that the ethers of aromatic hydroxy-aldehydes when acted on by concentrated nitric acid in the cold also underwent a similar reaction, the aldehyde group in part being displaced by the nitro-group. Piperonal, veratraldehyde, and myristicinaldehyde gave varying amounts of the corresponding nitrophenol ethers as well as the expected nitro-aldehydes. Anisaldehyde, however, only gave nitroanisaldehyde, and Salway pointed out that the accumulation of methoxyl groups resulted in an increased displacement of the formyl grouping.

That acetyl groups could be similarly displaced was observed by Harding and Weizmann (Trans., 1910, **97**, 1126), who by acting on 4:5-dimethoxy-*o*-methylacetophenone with nitric acid in warm glacial acetic acid solution obtained nitrohomocatechol dimethyl ether:

It was evident that these peculiar displacements were of more general occurrence than had formerly been supposed, and it was thought desirable to investigate the phenomena more closely, in order to see if any generalisation were possible, and also whether any means could be found of inhibiting the reaction, thus rendering possible the production in an easy and simple manner of the apparently more normal nitration products. In this connexion a careful study of the action of nitric acid on gallic acid trimethyl ether and the isomeric pyrogallolcarboxylic acid trimethyl ether has brought to light some interesting points.

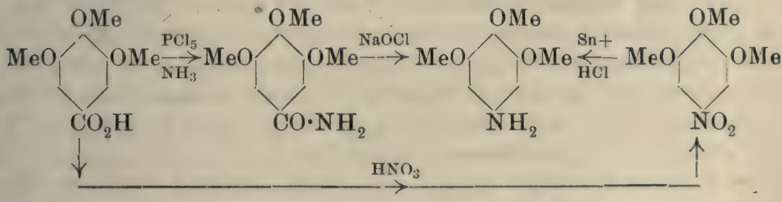
The action of nitric acid on gallic acid trimethyl ether has been investigated by Schiffer (*Ber.*, 1892, **25**, 721), who observed the displacement of the carboxyl group. Quite recently, and between the experimental results of the author and their publication, there appeared the communication of Thoms and Siebeling (*Ber.*, 1911, **44**, 2115) on the same subject. A thoroughly exhaustive examination of the products, however, does not appear to have been attempted. The action of nitric acid at 50—70°, the acid being either concentrated (D 1·4) or dilute, or in acetic acid solution, always gives a mixture of 5-nitropyrogallol trimethyl ether and nitrogallic acid trimethyl ether:



The largest yields of 5-nitropyrogallol trimethyl ether are obtained in acetic acid solution, and it is worthy of note that many of these displacements take place most readily when the nitration is carried out in that solvent. Thoms and Siebeling (*loc. cit.*), using fuming nitric acid in acetic acid solution, found that at $-15°$ the chief product was 5-nitropyrogallol trimethyl ether, whilst on warming 5:6-dinitropyrogallol trimethyl ether was obtained, nitration of the previously-formed mononitro-compound evidently taking place. The author has also found what is probably 5:6-dinitropyrogallol trimethyl ether among the nitration products. The compound melted at 118° (Thoms and Siebeling give 119°), and was insoluble in dilute alkalis. The point, however, is being re-investigated. It does not appear to have been previously observed that nitrogallic acid trimethyl ether is formed by the direct nitration of gallic acid trimethyl ether. The acid, however, has been prepared by Pollak and Feldscharek (*Monatsh.*, 1908, **29**, 135) by the hydrolysis of its ethyl ester, and again in exactly the same way by Thoms and Siebeling.

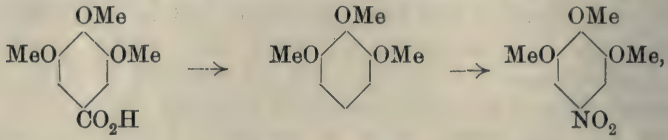
In addition to the above-mentioned compounds, there was isolated large amounts of oxalic acid, a dibasic acid, $C_{18}H_{17}O_{13}N$, and a very small amount of an acid melting at 154·5°. The question of the displacement of methoxyl groups by nitro-groups was also considered, but no evidence was obtainable that any such displacement had taken place.

The orientation of 5-nitropyrogallol trimethyl ether was accomplished by Graebe and Suter (*Annalen*, 1905, **340**, 222), thus proving that the nitro-group had displaced the carboxyl group, and that it had not arisen from the nitrogallic acid trimethyl ether by the elimination of carbon dioxide. The following scheme shows quite clearly the proof of the position of the nitro-group:



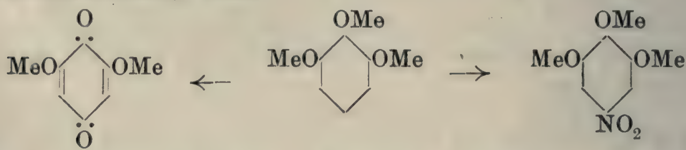
The present author has repeated this work, and confirmed it. In addition, two specimens of 5-acetylaminopyrogallol trimethyl ether were prepared from specimens of the base obtained by the two methods indicated in the diagram, and were found to be identical. Thus there can be no doubt that the action of nitric acid on gallic acid trimethyl ether results in the displacement of the carboxyl group by the nitro-group.

In considering displacements of groups of this kind by nitric acid, one obvious explanation suggests itself, namely, that the organic acid loses carbon dioxide, forming the parent phenol ether, which then undergoes substitution in the usual way:



and in the case of aldehydes and ketones that the side-chains, formyl and acetyl, undergo a preliminary oxidation to carboxyl. This view is borne out by the fact that carbethoxyl groups do not undergo this substitution. Salway (*loc. cit.*, p. 1159), however, has pointed out that, in the case of aldehydes, this view is untenable, and a consideration of the products of nitration of gallic acid trimethyl ether apparently points to the fact that it is also inadmissible in the case of organic acids, if gallic acid trimethyl ether can be taken as representative of this class of reaction.

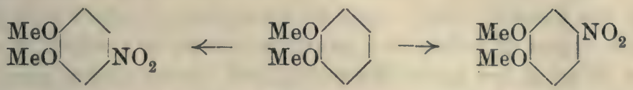
The action of nitric acid on pyrogallol trimethyl ether gives rise to a mixture of 3:5-dimethoxy-*p*-benzoquinone, as well as 5-nitropyrogallol trimethyl ether:



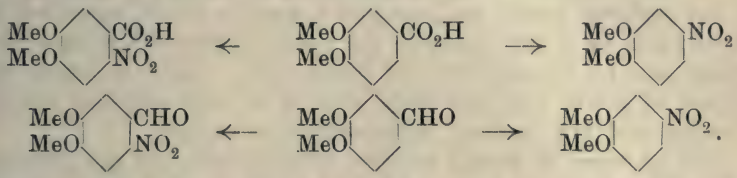
(Will, *Ber.*, 1888, **21**, 613; Schiffer, *Ber.*, 1892, **25**, 725; Graebe and Hess, *Annalen*, 1905, **340**, 232; Pollak and Goldstein, *Monatsh.*, 1908, **29**, 137). Formation of 3:5-diethoxy-*p*-benzoquinone also occurs during the nitration of pyrogallol triethyl ether (Pollak and Goldstein, *Monatsh.*, 1908, **29**, 137). If, then, there is during the production of 5-nitropyrogallol trimethyl ether from gallic acid trimethyl ether any intermediate formation of pyrogallol trimethyl ether, as such, it would be expected to show itself by the occurrence of 3:5-dimethoxy-*p*-benzoquinone among the products of nitration. This, however, is not the case; a most exhaustive search failed to reveal the presence of this quinone. Schiffer also states that the nitration of gallic acid trimethyl ether produces no quinone. It may be concluded then that the course of these reactions is one of direct substitution of the carboxyl or aldehyde group by the nitro-group.

In studying the rather scanty literature of reactions of this type, it was noticed that the substitution of the acyl group always gave rise to the same nitrophenol ether as that produced by the nitration

of the phenol ether itself. This is very clearly brought out if the substitution of veratrole is compared with that of its derivatives, veratric acid and veratraldehyde. The nitro-group enters either of the positions 4 or 5. In the case of veratrole this gives rise to the one derivative, 4- or 5-nitroveratrole:

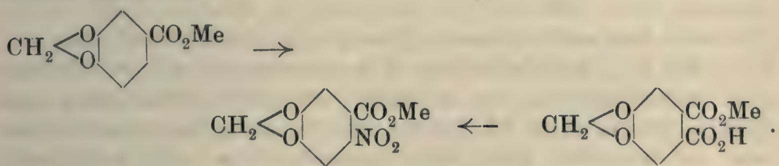


whereas in veratroles already substituted in positions 4 or 5 it gives rise to a mixture of nitro-compounds:



Homocatechol dimethyl ether and its ketone, 4:5-dimethoxy-*o*-methylacetophenone, give the same nitrohomocatechol dimethyl ether:

also methyl piperonylate and methyl hydrogen hydrastate show a similar behaviour:

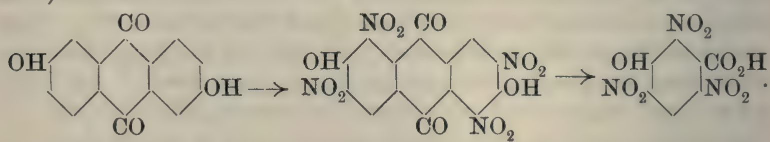


It would seem very probable from these examples that the substitution of acyl groupings by the nitro-group is conditioned by those forces in the molecule which direct the entrance of a nitro-group in the parent phenol ether, and that the substitution of the more complex group differs only in degree from that of hydrogen. That equal amounts of nitroveratric acid and nitroveratrole are not produced by the nitration of veratric acid is due to the more mobile hydrogen atom being more easily substituted than the heavier carboxyl. It must not be forgotten, however, that the carboxyl group itself exerts a definite directive influence as against that of the hydrogen atoms, but it would appear that its influence is small when compared with that of the methoxyl groups. The directive power of the two methoxyl groups in veratrole would appear to be sufficiently powerful to suppress that of certain other substi-

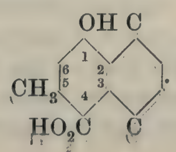
tuents, and to cause substitution to take place in the manner described.

One consequence of the displacement of acyl groups being similar to that of hydrogen is that the substitution of the more complex groups should obey those laws which govern the ordinary substitution in the benzene ring. Just as the action of nitric acid on the hydrogen atoms of substituted benzenes results in a selective action, and by doing so has given rise to the well known ortho-, para-, and meta-rules of substitution, so ought this selective action to be observed when the more complex groups are substituted. Thus, if the carboxyl group, etc., occupies a position which would not be substituted by a nitro-group in the parent phenol ether, then that group will be inactive towards nitric acid. Cases in which the action of nitric acid has been studied in this way are few in number, and are confined to derivatives of phenol.

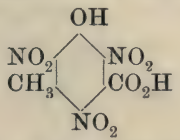
The positions in phenol reactive to nitric acid are the positions 2:4:6. Consequently it would be expected that groups occupying the positions 2:4:6 would be substituted by the nitro-group, and that those occupying the inactive positions 3:5 would remain unsubstituted; and this is found to be the case. Salicylic acid on continued nitration yields picric acid, the lighter and more mobile hydrogen atoms being first displaced, and finally the carboxyl group itself (Hübner, *Annalen*, 1879, **195**, 31; Hübner, Babcock, and Schaumann, *Ber.*, 1879, **12**, 1346; Schiff and Nasino, *Annalen*, 1879, **198**, 258; see also Beilstein, *Handbuch*, IV., 1490). Coumarin in a similar manner gives picric acid (Delaude, *Annalen*, 1843, **45**, 337), and derivatives of *p*-coumaric acid also on nitration yield *s*-trinitrophenol, for example, carthamine (Kametaka and Perkin, Trans., 1910, **97**, 1419). On the other hand, anthraflavic acid on nitration gives tetranitroanthraflavic acid, and finally 2:4:6-trinitro-*m*-hydroxybenzoic acid (Schardinger, *Ber.*, 1875, **8**, 1490):



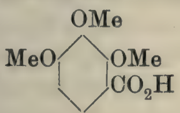
A still more striking example is the action of nitric acid on carminic acid, which contains the groupings:



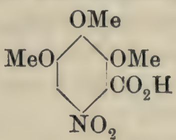
The groups occupying the active positions 2:4:6 are substituted by nitro-groups, either direct or after oxidation, whilst groups in the inactive positions 3:5 remain unsubstituted, and give rise to trinitrohydroxy-*m*-toluic acid (Kostanecki and Niementowski, *Ber.*, 1885, **18**, 253):



In order to gain more evidence on this important point it was deemed advisable to select a compound in which a carboxyl or aldehyde group occupied an inactive position in a molecule containing a large number of methoxyl groups, and to investigate the action of nitric acid on it under varying conditions. The presence of a large number of methoxyl groups would cause the carboxyl or aldehyde group to be more sensitive to the action of nitric acid (compare Salway, *loc. cit.*, p. 1159), and thus it would be possible to determine easily whether any substitution had taken place. The compound chosen was pyrogallolcarboxylic acid trimethyl ether (I):



(I.)

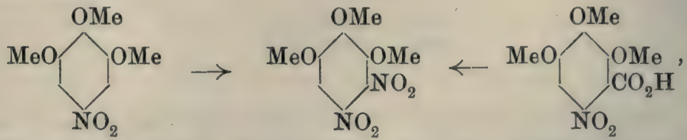


(II.)

The action of nitric acid on this compound does not appear to have been previously studied. The nitro-acid (II), however, has been prepared by Pollak and Goldstein (*Annalen*, 1907, **351**, 161) by nitrating methyl pyrogallolcarboxylate trimethyl ether, with subsequent hydrolysis.

The action of concentrated nitric acid in the cold, either alone or in acetic acid solution, results in the formation in almost quantitative yield of nitropyrogallolcarboxylic acid trimethyl ether. The use of the methyl ester of pyrogallolcarboxylic acid to prevent any possible carboxyl substitution taking place is unnecessary. The product obtained direct from the nitration of the free acid was completely soluble in sodium carbonate, and possessed the correct melting point. When, however, the action of hot nitric acid was investigated, it was found that a very small amount of a neutral substance was obtained, in addition to the nitro-acid. This melted at 118°, and was in all probability (see p. 1596) 5:6-dinitropyrogallol trimethyl ether. No trace of 6-nitropyrogallol trimethyl ether was observed. This compound has been prepared by Einhorn, Cobliner, and Pfeiffer (*Ber.*, 1904, **37**, 117), and melts at 44°

(compare also Thoms and Siebeling, *loc. cit.*). The formation of 5:6-dinitropyrogallol trimethyl ether is in accordance with the views expressed in this paper; the carboxyl group in nitropyrogallolcarboxylic acid trimethyl ether occupies the position in 5-nitropyrogallol trimethyl ether active towards a nitro-group, and is in consequence substituted:



whereas when not occupying the inactive position as in pyrogallolcarboxylic acid trimethyl ether, it remains unaffected by the nitric acid, although the isomeric gallic acid trimethyl ether undergoes substitution in a very marked manner.

It would seem very probable, then, by these examples that the substitution of acyl groups is governed by the same forces in the benzene nucleus which control the substitution of the hydrogen atoms in the parent phenol ether. The groups ·H, ·CHO, ·CO, $\cdot CH_3$, $\cdot CO_2H$ apparently form a series, any member of which can be substituted by the group $\cdot NO_2$. It remains to be seen how far this series can be extended, and work is in progress to determine this point. As regards the actual mechanism of the substitutions, it is of interest to note that if the nitrations are carried out in the cold in presence of a trace of hydrogen peroxide, the expected substitution does not take place. Gallic acid trimethyl ether, on treatment with concentrated nitric acid in presence of a trace of hydrogen peroxide, does not yield any 5-nitropyrogallol trimethyl ether. This interesting observation, which may turn out to be of great practical utility, is at present being studied, and the results will shortly be laid before the Society.

Experimental.

Action of Nitric Acid on Gallic Acid Trimethyl Ether.

In order to investigate thoroughly the action of nitric acid on gallic acid trimethyl ether, and to observe if any formation of 3:5-dimethoxy-*p*-benzoquinone occurred, the reaction was carried out under the following conditions.

I.—Fifty grams of gallic acid trimethyl ether were added in small quantities at a time to 100 c.c. of concentrated nitric acid (D 1·4). A vigorous reaction took place with rise of temperature, carbon dioxide and nitrous fumes being rapidly evolved. The temperature, however, was not allowed to rise above 50°. When

all the gallic acid trimethyl ether had been added, the reaction was completed by allowing the mixture to remain at room temperature for an hour. It was then diluted with water, and the precipitated substances were collected. The 5-nitropyrogallol trimethyl ether (A) was purified from the accompanying carboxylic acids by dissolving the latter in dilute sodium carbonate solution, and washing the residue well with water. In this way there was obtained 9·5 grams of 5-nitropyrogallol trimethyl ether. The sodium carbonate washings on acidification yielded 7 grams of an acid mixture (B) (p. 1595).

II.—Gallic acid trimethyl ether was heated with dilute nitric acid (1 : 4) until the vigorous reaction which set in had subsided. In this case the temperature was not allowed to rise above 70°. The solid products which separated on cooling were collected, and treated as described in method I. Fifty grams of gallic acid trimethyl ether in this manner gave 11 grams of crude 5-nitropyrogallol trimethyl ether (A) and 2 grams of an acid mixture (B).

III.—In this case gallic acid trimethyl ether was dissolved in glacial acetic acid, and an excess of nitric acid added. The reaction again was very vigorous, but the yield of neutral compounds obtained on dilution was much larger under these conditions. From 50 grams of gallic acid trimethyl ether were obtained 26 grams of crude neutral compounds (A) and 8 grams of an acid mixture (B).

The filtrates (C) from these nitration experiments were mixed and investigated as described on page 1596.

Examination of 5-*Nitropyrogallol Trimethyl Ether* (A).

The whole of the crude 5-nitropyrogallol trimethyl ether obtained from the above-described experiments was purified by crystallisation from absolute alcohol, from which it separated quite readily in the characteristic pale yellow needles, melting at 99°. The residues on complete evaporation of the alcohol yielded a small amount of a substance, which when crystallised from dilute acetic acid melted at 88—89°. When freshly prepared it consisted of almost colourless needles, which on drying and exposure to light were converted into a yellow, amorphous-looking powder. The amount, however, was too small to permit of further investigation, and it is very doubtful if a pure substance was isolated.

Gallamide Trimethyl Ether, $C_6H_2(OMe)_3 \cdot CO \cdot NH_2$.

This compound has been previously prepared by the methylation of gallamide (Marx, *Annalen*, 1891, **263**, 250), and by passing dry

ammonia gas into a benzene solution of gallyl chloride trimethyl ether (Graebe and Suter, *Annalen*, 1905, **340**, 222). Its preparation, however, is easily effected by pouring a large excess of concentrated aqueous ammonia on to freshly prepared powdered gallyl chloride trimethyl ether, when the amide separates as a white, insoluble solid. It is collected, washed with cold water, and purified by crystallisation from 90 per cent. alcohol. It melts at 157°. (Found, N = 6·7. Calc., N = 6·6 per cent.)

5-Acetylaminopyrogallol Trimethyl Ether,
$C_6H_2(OMe)_3 \cdot NH \cdot CO \cdot CH_3$.

The base 5-aminopyrogallol trimethyl ether was prepared (*a*) by the action of freshly prepared sodium hypochlorite on gallamide trimethyl ether (Graebe and Suter, *Annalen*, 1905, **340**, 222); (*b*) by the reduction of 5-nitropyrogallol trimethyl ether (Will, *Ber.*, 1888, **21**, 613).

A mixed melting-point determination made with specimens of the base prepared by both methods gave the same melting point as that shown by each constituent. 5-Acetylaminopyrogallol trimethyl ether is easily obtained by warming the base with acetic anhydride on the water-bath for an hour, cooling, and then pouring into water. It crystallises from alcohol in small needles, which soften at 110°, and finally melt at 127°, and contains one molecule of water of crystallisation:

0·1354 gave 0·2676 CO_2 and 0·0812 H_2O. C = 53·9; H = 6·6.
0·1434 „ 7·5 c.c. N_2 (moist) at 20° and 756 mm. N = 5·9.
$C_{11}H_{15}O_4N,H_2O$ requires C = 54·3; H = 6·9; N = 5·7 per cent.

A direct determination of the water of crystallisation does not give a very satisfactory result, as even when kept at 100° there is considerable decomposition if the heating is continued for any length of time. The figures, however, show the presence of one molecule of water of crystallisation if the rate of the loss of water is taken into account:

0·2997, on heating at 101° for one hour, lost 0·0214.
0·2997, „ „ 101° „ two hours, „ 0·0224.

Loss at end of first hour = 7·2 per cent.
„ „ second „ = 8·2 „
$C_{11}H_{15}O_4N,H_2O$ requires loss = 7·4 per cent.

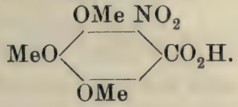
The acetyl group is not hydrolysed by warm dilute aqueous potassium hydroxide.

The same acetyl derivative is produced from specimens of base prepared by either methods (*a*) or (*b*). This was confirmed by the

method of mixed melting point. Graebe and Suter (*loc. cit.*) give the melting point of 5-acetylaminopyrogallol trimethyl ether as 124°, but no analysis of their product is given.

Examination of the Acid Mixture (B).

Isolation of Nitrogallic Acid Trimethyl Ether,



The crude acid mixtures from the three previously described nitration experiments (p. 1593) were mixed together, and the nitrogallic acid trimethyl ether was separated from its accompanying impurities by crystallisation from benzene, it being almost insoluble in the cold solvent. It was identified by means of its melting point (163—164°) and analysis. (Found, C=46·7; H=4·1. Calc., C=46·6; H=4·2 per cent.)

This acid has previously been described by Pollak and Feldscharek (*Monatsh.*, 1908, **29**, 139), who obtained it by the hydrolysis of its ethyl ester, a compound prepared by the nitration of ethyl gallate trimethyl ether. It seems, however, to have escaped observation that it is one of the products of the direct nitration of gallic acid trimethyl ether.

Nitrogallic acid trimethyl ether is esterified only with great difficulty.

Nitrogallamide trimethyl ether is readily prepared by mixing nitrogallic acid trimethyl ether with a small excess of phosphorus pentachloride in presence of a little benzene and warming slightly. A gentle reaction sets in, and at the end of two hours the semi-solid mass is poured into a large excess of concentrated aqueous ammonia, when the amide separates as a solid mass. It crystallises from alcohol in pulpy masses of needles, melting at 182—184°:

0·1339 gave 0·2323 CO_2 and 0·0529 H_2O. C=47·3; H=4·4.

$C_{10}H_{12}O_6N_2$ requires C=46·9; H=4·6 per cent.

Isolation of an Acid, $C_{18}H_{17}O_{13}N$.

The benzene mother liquors from the separation of the nitrogallic acid trimethyl ether were evaporated to a small bulk, and an equal volume of light petroleum was added. The yellow precipitate which formed was collected and purified by crystallisation from water until further crystallisation ceased to alter its melting point. The acid separates from water in almost colourless nodules, which rapidly turn yellow on exposure to light, and melt at 136—137°:

0·1297 gave 0·2245 CO_2 and 0·0435 H_2O. C=47·2; H=3·7.
0·1591 „ 4·8 c.c. N_2 (moist) at 24° and 756 mm. N=3·3.
$C_{18}H_{17}O_{13}N$ requires C=47·5; H=3·9; N=3·1 per cent.

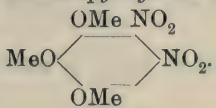
A determination of the basicity gave the following results:

0·1307 required for neutralisation 0·0223 NaOH, whilst the same weight of a dibasic acid, $C_{18}H_{17}O_{13}N$, requires 0·0227 NaOH.

Examination of the Filtrate (C).

The aqueous residues from the nitration of gallic acid trimethyl ether, amounting to about two litres, were combined and evaporated on the water-bath to about half their bulk, and then set aside in a cold air chamber to crystallise. After keeping overnight, a mass of crystals separated, which on collection was found to consist of oxalic acid mixed with a small amount of the acid $C_{18}H_{17}O_{13}N$ (p. 1595), the two acids being easily separated by means of warm water. A further evaporation and cooling resulted in the separation of more oxalic acid, but in this case free from the acid $C_{18}H_{17}O_{13}N$. In all, there were isolated about forty grams of oxalic acid.

Isolation of 5 : 6-*Dinitropyrogallol Trimethyl Ether,*



The remaining nitric acid was then removed by repeated evaporation and dilution, when there gradually separated a very small amount of a colourless, flocculent precipitate. This, on crystallisation from alcohol or acetic acid, melted constantly at 118°, and any further treatment failed to alter its properties. Thoms and Siebeling give the melting point of 5 : 6-dinitropyrogallol trimethyl ether as 119°, and state that the melting point given by Will (126°) is too high. As the compound (m. p. 118°) agreed in properties with the 5 : 6-dinitropyrogallol trimethyl ether described by Thoms and Siebeling (*Ber.*, 1911, **44**, 2123), this, taken in conjunction with the method of preparation and the fact that the same compound is also formed by the action of hot nitric acid on pyrogallolcarboxylic acid trimethyl ether (see p. 1597), is taken provisionally as evidence of its constitution. The point, however, will be re-investigated.

Isolation of an Acid Melting at 154·5°.—The residues after the separation of the above-described substance were evaporated to dryness, triturated with cold sodium carbonate solution, and

filtered. The filtrate on acidifying slowly deposited a small quantity of an acid, which after two crystallisations from water melted sharply at 154·5°. The amount, however, was too small to permit of further investigation.

Thus from 150 grams of gallic acid trimethyl ether there was obtained nearly 110 grams of products, and a most exhaustive search had failed to detect the presence of 3:5-dimethoxy-*p*-benzoquinone, even in the slightest trace. Under conditions identical with those obtaining in the experiments just described, the action of nitric acid on pyrogallol trimethyl ether yielded large amounts of this quinone (compare Graebe and Hess, *Annalen*, 1905, **340**, 232).

Action of Nitric Acid on Pyrogallolcarboxylic Acid Trimethyl Ether.

The action of nitric acid on pyrogallolcarboxylic acid trimethyl ether was studied under the following conditions:

I.—Two grams of acid were dissolved in excess of concentrated nitric acid, and the solution kept cold by a stream of water. There is no violent reaction, as in the case of gallic acid trimethyl ether. At the end of fifteen minutes water was added, and the clear liquid was allowed to remain for some hours in the cold air chamber, when there slowly separated a mass of faintly yellow crystals. These were found to be completely soluble in cold dilute sodium carbonate solution, and a melting-point determination showed them to consist of pure nitropyrogallolcarboxylic acid trimethyl ether.

II.—Two grams of the acid were dissolved in acetic acid, and to this solution was added the nitric acid, the whole being allowed to remain at room temperature for fifteen minutes. The crystalline product which separated on dilution was found to consist entirely of nitropyrogallolcarboxylic acid trimethyl ether. No neutral compounds were observed.

III.—The action of hot concentrated nitric acid on pyrogallolcarboxylic acid trimethyl ether, however, results in the production of a very small amount of a substance insoluble in cold dilute sodium carbonate solution, as well as the nitro-acid. From two grams of pyrogallolcarboxylic acid trimethyl ether there was obtained enough neutral substance to permit of its crystallisation and a determination of the melting point. It crystallised from alcohol in colourless needles, melting at 118°, and was found to be identical with the 5:6-dinitropyrogallol trimethyl ether obtained by the nitration of gallic acid trimethyl ether (p. 1596).

The aqueous residues from the above experiments were mixed together and evaporated on the water-bath. These separated from

the solution a further amount of 6-nitropyrogallolcarboxylic acid trimethyl ether. The mother liquors were then completely evaporated, and the small residue was extracted with cold dilute sodium carbonate solution. This on acidifying yielded a small amount of an acid, which softened at 90°, and finally melted at 100°.

In conclusion, I desire to thank the Research Fund Committee of the Chemical Society for the grant which has defrayed the cost of this investigation, and also to thank Dr. J. W. Walker for the kindly interest he has taken during the progress of this work.

MacDonald Chemistry and Mining Building,
McGill University, Montreal.

CLXXX.—*Trialkylammonium Nitrites and Nitrites of the Bases of the Pyridine and Quinoline Series. Part II.*

By Pañchānan Neogi, M.A.

α-Picolinium Nitrite.

An ice-cold solution of α-picoline hydrochloride was treated with silver nitrite in a bottle immersed in melting ice. The filtered solution did not liberate any iodine on the addition of potassium iodide, but on the addition of an acid, iodine was copiously set free. The volume of nitrogen obtained by the "urea" method was identical with the volume of nitric oxide obtained by the Crum-Frankland method, showing that a pure nitrite was formed in the solution. Very little free nitrous acid was present in the cold solution, as practically no nitrogen was evolved by treating an aliquot part of the liquid with carbamide alone in the Crum nitrometer without the addition of dilute sulphuric acid.

An ice-cold alcoholic solution of the nitrite when evaporated to dryness in a vacuum desiccator over sulphuric acid, surrounded with broken ice, yielded colourless, needle-shaped crystals, which on examination were found to consist of a mixture of α-picolinium nitrite and nitrate.

Quinolinium Nitrite.

An ice-cold solution of the nitrite was prepared in the same manner as above. No iodine was set free on the addition of potassium iodide alone, but on the addition of a dilute acid, iodine

was copiously liberated. The cold solution gave equal volumes of nitrogen and nitric oxide by the "urea" and Crum-Frankland methods. A small quantity of nitrogen was collected when an aliquot part of the cold solution was treated with carbamide without the addition of dilute sulphuric acid, showing the presence of very small quantities of free nitrous acid.

An ice-cold solution of the nitrite when evaporated in a vacuum desiccator over sulphuric acid surrounded with broken ice gave a liquid which was found to be quinoline. The nitrite which undoubtedly exists in solution has not been obtained in the solid condition.

Piperidinium Nitrite, C_5NH_{11},HNO_2.

Ray and Rakshit (Proc., 1911, **27**, 71) have prepared dimethylammonium nitrite, a nitrite of a secondary alkylamine. Experiments were undertaken to see if piperidine, a secondary base of the pyridine series, would form a nitrite. The hydrochloride of the base was treated as usual with silver nitrite at the ordinary temperature. The resulting solution was neutral, and copiously liberated iodine on the addition of an acidified solution of potassium iodide. The solution could be concentrated on the water-bath to a small bulk, and when evaporated to dryness in a vacuum desiccator over sulphuric acid yielded colourless plates. The crystals were extremely hygroscopic, very soluble in water or alcohol, but very sparingly so in ether. The salt was fairly stable, and on keeping in the desiccator remained unchanged for a long time. The salt was analysed by the "urea" method:

0·4108 gave 76·0 c.c. N_2 (made up to 20 c.c. with water, of which 1 c.c. = 3·8 c.c. N_2) at 27° and 750 mm. N("nitritic") = 10·05.

$C_5H_{11}N,HNO_2$ requires N("nitritic") = 10·6 per cent.

Sublimation and Decomposition of Piperidinium Nitrite.

The crystals were heated under diminished pressure in a long tube immersed in a sulphuric acid bath. When the temperature was about 75° and the pressure was 10—20 mm., small crystals began to appear in the upper part of the tube. The temperature was kept between 80° and 100°, when the salt slowly sublimed to form a white crust on the upper part of the tube. The sublimed salt was found to be piperidinium nitrite.

When, however, the temperature was raised to 110° the salt began to melt, and at 120° the whole of it was turned into a reddish-yellow liquid. The temperature was raised to 140° in order to ensure the complete decomposition of the nitrite. The liquid was moderately soluble in water, readily gave Liebermann's reaction,

and boiled with charring at about 215°. The liquid was thus nitrosopiperidine. The decomposition of piperidinium nitrite is represented by the following equation:

$$C_5H_{11}N,HNO_2 = C_5H_{10}N\cdot NO + H_2O.$$

Ray and Rakshit (Proc., 1911, **27**, 122) have shown that dimethylammonium nitrite decomposes on heating, forming nitrosodimethylamine, although without sublimation. Piperidinium nitrite was found to volatilise with steam under diminished pressure in appreciable quantities.

Pyridine Methonitrite, $C_5H_5N,CH_3\cdot NO_2$.

The bases of this series form additive compounds with alkyl iodides. The following experiments show that these additive products yield nitrites of a fairly stable character. The iodides should be prepared at the time of the preparation of the nitrites, as otherwise they gradually turn yellow and then red on keeping for some days.

A solution of pyridine methiodide was treated with silver nitrite in the usual manner. The filtered solution was neutral, and liberated iodine copiously from an acidified solution of potassium iodide. The solution could be concentrated to a small bulk on the water-bath, and when kept in a vacuum desiccator over sulphuric acid gave a reddish-yellow liquid, which was found on analysis to be pyridine methonitrite:

0·5404 gave 98·0 c.c. N_2 (made up to 20 c.c. with water, of which 1 c.c. = 4·9 c.c. N_2) at 27° and 752 mm. N("nitritic") = 9·8.

$C_5H_5N,CH_3\cdot NO_2$ requires N(nitritic) = 10·0 per cent.

The nitrite was very soluble in water or alcohol, and almost insoluble in ether.

Piperidine Methonitrite, $C_5NH_{11},CH_3\cdot NO_2$.

The solution of the nitrite was prepared in the usual manner. It was neutral, and could be concentrated on the water-bath to a small bulk. On evaporating the solution to dryness in a vacuum desiccator over sulphuric acid, the nitrite was obtained in colourless plates:

0·1766 gave 32·0 c.c. N_2 (made up to 10 c.c. with water, of which 1 c.c. = 3·2 c.c. N_2) at 28° and 754 mm. N("nitritic") = 9·8.

$C_5H_{11}N,CH_3\cdot NO_2$ requires N("nitritic") = 9·5 per cent.

The crystals were extremely hygroscopic, very soluble in water and alcohol, and sparingly so in ether.

Picoline Methonitrite, $CH_3{\cdot}C_5NH_4,CH_3{\cdot}NO_2$.

The solution as prepared in the usual way was colourless, but on evaporation to a small bulk on the water-bath or in a vacuum desiccator over sulphuric acid gave a red liquid, which ultimately solidified to red fibrous crystals. The red colour is due to the presence of an impurity, and the crystals are really colourless:

0·2024 gave 32·0 c.c. N_2 (made up to 10 c.c. with water, of which 1 c.c. = 3·2 c.c. N_2) at 27° and 750 mm. N("nitritic") = 8·59.

$C_6H_7N,CH_3{\cdot}NO_2$ requires N("nitritic") = 9·09 per cent.

The crystals were very hygroscopic, very soluble in water or alcohol, and insoluble in ether.

Quinoline Methonitrite, $C_9NH_7,CH_3{\cdot}NO_2$.

The solution of this nitrite was at first colourless, but during concentration and exposure to air gradually changed to orange, then red, and finally dark red. The crystals of the same colour obtained in the vacuum desiccator were very hygroscopic, very soluble in water or alcohol, and sparingly so in ether:

0·1540 gave 15·9 c.c. N_2 at 27° and 750 mm. N("nitritic") = 5·6.

$C_9H_7N,CH_3{\cdot}NO_2$ requires N("nitritic") = 7·3 per cent.

The low value is due to liberation of carbon.

The action of heat on these compounds is being studied, and the examination of other nitrites of this series is being continued.

Chemical Laboratory, Rajshahi College,
Rajshahi, Eastern Bengal, India.

CLXXXI.—*Ionisation in Non-aqueous Solvents. Part I.*

By Harry Medforth Dawson and May Sybil Leslie, M.Sc.

In this paper an account is given of observations which show the occurrence of unexpected ionisation phenomena in non-aqueous solutions of perhalogen salts. The nature of the solutions, which are obtained when iodides of the alkali metals or ammonium radicles together with iodine are dissolved in nitrobenzene, has already been examined in some detail, and evidence in favour of the existence of definite polyiodides of the types MI_3, MI_5, MI_7, and MI_9 has been adduced (Dawson, Trans., 1908, **93**, 1308). Such polyiodide solutions are good conductors of electricity, and by

means of conductivity and freezing-point measurements, the degree of ionisation of the various polyiodides was determined (Dawson and Jackson, Trans., 1908, **93**, 2063).

The collected data for nitrobenzene solutions (*loc. cit.*, p. 2068) indicate that in 0·1 molar solution the conductivity decreases slightly from the tri-iodide to the ennea-iodide, the decrease corresponding with the diminishing mobility of the polyiodide anion as its complexity increases. On the other hand, observations made with tetrapropylammonium iodide, which is the only iodide examined which is readily soluble in nitrobenzene, show that the conductivity of the simple iodide is somewhat smaller than that of the corresponding polyiodides. A similar, but much larger, difference was obtained with sodium, ammonium, potassium, rubidium, and cæsium iodides when small quantities of ethyl alcohol were added to the nitrobenzene in order to obtain a solvent capable of dissolving the simple iodides sufficiently to yield 0·005 molar solutions.

These observations appeared to warrant a further inquiry into the conductivity and ionisation relationships of the simple and polyiodides in other organic solvents. Measurements of the conductivity have therefore been made in methyl alcohol, ethyl alcohol, methyl acetate, ethyl acetate, benzonitrile, nitromethane, nitrobenzene, and acetic acid solutions. Potassium iodide was chiefly used as electrolyte, although a few measurements were made with tetraethyl- and tetrapropyl-ammonium iodide.

In the following tables the conducting powers of the various solutions at 18° are expressed as molecular conductivities, and values are recorded for solutions in which the molar ratio of iodine to iodide (I_2/MI) was respectively 0, 0·5, 1, 2, 3, 4, or some higher number. The solvent, the iodide, and its molar concentration are indicated at the head of each table.

Methyl Alcohol.

0·1 Molar potassium iodide.

Ratio I_2/KI	0	0·5	1	2	3	4	7
Molecular conductivity...	62·4	66·6	67·0	64·0	60·4	58·9	54·9

0·01 Molar potassium iodide.

Ratio I_2/KI	0	0·5	1	2	3	4	7
Molecular conductivity...	82·5	84·4	85·4	84·0	82·7	81·5	78·4

0·01 Molar tetrapropylammonium iodide.

Ratio $I_2/N(C_3H_7)_4I$.........	0	1	2
Molecular conductivity...	73·5	64·7	61·4

Polyiodides were found to be precipitated from the methyl alcohol solution of the tetrapropylammonium salt when larger quantities of iodine were added.

Ethyl Alcohol.

0·05 Molar potassium iodide.

Ratio I_2/KI	0	0·5	1	2	3	4	7
Molecular conductivity...	22·2	27·8	32·8	31·7	31·5	30·1	28·9

0·01 Molar potassium iodide.

Ratio I_2/KI	0	0·5	1	2	3	4	7
Molecular conductivity...	29·6	34·0	38·3	38·6	37·8	37·2	36·2

From ethyl alcoholic solutions of the substituted ammonium iodides, polyiodides were precipitated on the addition of relatively small quantities of iodine, and comparative measurements could not therefore be made in these cases.

Methyl Acetate.

0·01 Molar potassium iodide.

Ratio I_2/KI	0	0·5	1	2	3	4	7
Molecular conductivity...	1·15	9·85	16·2	22·4	24·6	25·7	27·3

Ethyl Acetate (moist).

0·01 Molar potassium iodide.

Ratio I_2/KI	0	0·5	1	2	3	4	7
Molecular conductivity...	0·38	5·45	9·0	13·7	16·0	17·0	18·4

In order to obtain a 0·01 molar solution of the iodide, it was necessary to add a little water to the ethyl acetate, and the solvent used in this series of measurements contained about 1·3 volumes per cent. of water.

Ethyl Acetate (saturated with water at 18°).

0·1 Molar potassium iodide.

Ratio I_2/KI.....................	0	1	2	3	4	5
Molecular conductivity	—	15·7	22·7	24·4	25·9	26·7

These measurements were made because of the fact that experiments relating to the chemical dissociation of the polyiodides in ethyl acetate solution were carried out, as will be seen later, with this concentration, and with solutions saturated with water.

Benzonitrile.

0·01 Molar tetraethylammonium iodide.

Ratio $I_2/N(C_2H_5)_4I$............	0	0·5	1	2	3	4
Molecular conductivity......	31·1	32·9	35·0	34·3	33·6	33·3

Nitromethane.

0·01 Molar tetraethylammonium iodide.

Ratio $I_2/N(C_2H_5)_4I$............	0	0·5	1	2	3	4
Molecular conductivity......	86·7	86·5	85·7	82·0	79·4	77·4

Nitrobenzene.

0·01 Molar potassium iodide.

Ratio I_2/KI	0	1	2	3	4	7
Molecular conductivity......	(19)	27·0	28·1	28·8	29·2	29·7

According to Euler (*Zeitsch. physikal. Chem.*, 1899, **28**, 622), the molecular conductivity of potassium iodide in nitrobenzene at concentrations of 0·001, 0·0005, and 0·00025 mol. per litre is 19, 19, and 19·5 respectively. According to these numbers, the molecular conductivity does not vary appreciably with the dilution, and therefore it may be assumed that 19 is the approximate value of the conductivity of the 0·01 molar iodine-free solution, which, of course, cannot be prepared by reason of the slight solubility of the salt.

Acetic Acid.

0·01 Molar potassium iodide.

Ratio I_2/KI	0	1	2	3	4
Molecular conductivity...	—	2·08	3·05	3·6	3·05

Before entering into a discussion of the relationships which are exhibited by the foregoing data, reference may be made to the question of polyiodide formation in the various solvents. In the case of aqueous solutions, irrefutable evidence in favour of the existence of tri-iodides has been brought forward, and various facts point to the formation of higher polyiodides as the concentration of the solution increases. From the value of the constant for the equilibrium $KI_3 \rightleftarrows KI + I_2$ in aqueous solution, it can be shown that in a 0·1 molar solution of the tri-iodide this would be dissociated to the extent of about 10 per cent., and in 0·01 molar solution to about 35 per cent. The chemical dissociation of the higher polyiodides is very much greater, and on this account water represents a solvent which is relatively unfavourable to the formation of perhalogen compounds.

On the other hand, nitrobenzene is a solvent in which chemical dissociation of the polyiodides takes place to only a very limited extent, and on this account it has been possible to show the formation of definite compounds of the types MI_3, MI_5, MI_7, and MI_9 in such solutions. The similarity in the solubility relationships (Dawson, Trans., 1904, **85**, 467) exhibited by other organic solvents in comparison with nitrobenzene supports the view that more or less stable polyiodides of the same kind are also formed in these solutions. For an actual proof of this it would be necessary to carry out series of measurements similar to those which have already been made in the case of nitrobenzene. Such experiments would afford information relative to the degree of stability of the polyiodides in the different solvents; but this problem was obviously beyond the scope of the present investigation, and on this account it was considered sufficient to examine the polyiodide formation in one only of the solvents other than nitrobenzene. Ethyl acetate was chosen for this purpose, partly in consequence of the remarkable increase which takes place in the conductivity as the relative proportion of iodine to iodide increases, and also because of the fact that this solvent is only partly miscible with water.

The method employed in the test for dissolved polyiodides was essentially the same as that already described in the investigation of nitrobenzene solutions (Trans., 1908, **93**, 1312). Potassium iodide and iodine were dissolved in ethyl acetate, previously saturated with water at 18°, the quantities of substance weighed out being such as to give 0·1 molar solutions of the composition $(KI+I_2)$, $(KI+2I_2)$, $(KI+3I_2)$, and $(KI+4I_2)$. Portions of each of these solutions were then carefully shaken up at 18° with appropriate quantities of a solution containing the equilibrium amount of potassium iodide dissolved in water, which had been previously saturated with ethyl acetate at the same temperature.

When the shaking, incidental to the attainment of equilibrium between the two layers of liquid, is carried out in such a way that very small drops are not formed, there is no difficulty attaching to the distribution experiments in the case of the first three solutions. The solution of the composition 0·1 molar $(KI+4I_2)$ is, however, very nearly of the same density as the corresponding aqueous solution, and although separation takes place after the preliminary agitations, it was found that the two layers soon coalesced to form a homogeneous liquid. On this account, the experiments with the $(KI+4I_2)$ solution were not carried to completion. A similar coalescence was observed later in the case of the ethyl acetate solution containing iodine and potassium iodide in the ratio $3I_2:KI$. After about a fortnight, during which this

solution was allowed to remain in contact with its equilibrium aqueous solution, the two liquids, although originally of appreciably different density, were found to have given rise to a single solution. This rather curious phenomenon has not been further investigated as yet.

From the iodide and total iodine concentrations of the equilibrium aqueous solutions, it is possible to calculate the concentration of free iodine by means of the constant for the equilibrium $KI_3 \rightleftarrows KI + I_2$. At 18°, $K = [KI][I_2]/[KI_3]$ is equal to 0·00115. It seems likely, however, that the presence of ethyl acetate in the aqueous solution will alter to some extent the value of this constant, and for this reason the free iodine concentration can only be estimated approximately.

The following table contains the data:

	Composition of aqueous solutions in equilibrium with the ethyl acetate solutions.		
Composition of ethyl acetate solutions.	Mols. KI per litre.	Mols. iodine per litre.	Mols. free iodine per litre.
0·1 mol. $(KI+I_2)$	2·3	0·00010	0·00000005
0·1 ,, $(KI+2I_2)$	0·025	0·0015	0·00007
0·1 ,, $(KI+3I_2)$	0·008	0·0008	0·00011

On account of the uncertainty attaching to the iodine distribution ratio, the question of polyiodide formation is most conveniently examined by reference to the data in the fourth column of the table. If the order of magnitude of the iodine distribution ratio (about 200) is taken into consideration, it is evident that these numbers indicate that the first ethyl acetate solution contains a very stable tri-iodide, and that the other two contain respectively penta- and hepta-iodide, which are chemically dissociated to but a comparatively small extent.

In thus favouring the formation of polyiodides, ethyl acetate is very similar to nitrobenzene, and it is probable that compounds of the same series are formed in both solvents. As already mentioned, there are also good grounds for the assumption that similar polyhalogen compounds are formed in the other solvents which have been examined in regard to their electrical conductivity.

Returning to the consideration of the electrical conductivities of the iodide and polyiodide solutions, it may be noticed that in nearly every instance the conductivity increases on passing from the iodide to the tri-iodide. In certain cases, for example, the 0·05 molar solutions in ethyl alcohol, this increase is followed by a decrease of conductivity on passing to the higher polyiodides, whilst in others, such as the methyl and ethyl acetate solutions, the higher polyiodides conduct very much better than the tri-iodide.

The relationships involved are clearly shown by means of the curves which are obtained when the molecular conductivity is plotted as a function of the iodine concentration. For two typical cases they are sufficiently evident from the following table, in which the conductivities of the various polyiodide solutions are expressed in terms of the conductivity of the iodide solution which is made equal to unity.

Relative Conductivities of 0·05 *Molar Solutions in Ethyl Alcohol.*

KI.	KI_3.	KI_5.	KI_7.	KI_9.
1	1·48	1·43	1·42	1·36

Relative Conductivities of 0·01 *Molar Solutions in Moist Ethyl Acetate.*

KI.	KI_3.	KI_5.	KI_7.	KI_9.
1	23·7	36·0	42·1	44·7 *

* It is probably safe to infer that these ratios would be still greater in the case of anhydrous ethyl acetate.

The variations in conductivity which are found in these cases may be conveniently compared with those exhibited by aqueous solutions. On the addition of successive quantities of iodine to an aqueous solution of potassium iodide, the conductivity decreases in a regular manner. Since the iodide and tri-iodide, which are alone involved in the case of the aqueous solution, are equally ionised (Dawson, Trans., 1901, **79**, 238; Burgess and Chapman, Trans., 1904, **85**, 1305; Bray and MacKay, *J. Amer. Chem. Soc.*, 1910, **32**, 914), the observed fall in conducting power is due to the smaller mobility of the tri-iodide as compared with that of the iodide ion. As a result of this diminished mobility, the conductivity of the tri-iodide is about 25 per cent. smaller than that of the iodide.

A similar influence of increasing anionic complexity may be expected in non-aqueous solvents, although the magnitude of the effect may be somewhat different. In contrast with aqueous solutions, however, the conductivity of potassium tri-iodide in the non-aqueous solutions is generally greater, and in certain cases enormously greater, than that of the iodide. In methyl and ethyl acetates, the conductivity of the higher polyiodides is also very much larger than that of the tri-iodide.

There can be little doubt * that the observed variations in

* The fact that liquid iodine yields good conducting solutions when potassium iodide is dissolved in it (Lewis and Wheeler, *Zeitsch. physikal. Chem.*, 1906, **56**, 179) cannot have much influence on the conductivities with which we are concerned.

conductivity are due to differences in the extent to which the various electrolytes are ionised, and it is evident that in certain solvents these differences are remarkably large.

The proof that the polyiodides of the alkali metals are ionised to a much greater extent than the simple iodides in certain solvents, is of particular interest in connexion with Walden's idea of a "normal" electrolyte (*Zeitsch. physikal. Chem.*, 1906, **54**, 129). This conception is in agreement with the fact that, in a given solvent, different binary salts of the type $M^{\cdot}X'$ are ionised to nearly the same extent when the solutions are dilute. At moderate dilutions differences are exhibited by the individual salts, but these are very small in comparison with the vast differences in the extent to which the alkali iodides and the corresponding polyiodides are ionised in solvents such as methyl and ethyl acetate. The simple iodides, when dissolved in these esters, behave like weak electrolytes in comparison with the polyiodides. The corresponding differences between the iodides and polyiodides of the tetra-substituted ammonium bases are probably much smaller, as in the case of nitrobenzene solutions (Dawson and Jackson, Trans., 1908, **93**, 2071) which have been examined previously. For this solvent, the conductivity data indicate that the polyiodides of the alkali metals are normally ionised, and if this is true for other solvents, as seems very probable, it follows that the ionisation of the alkali metal iodides is abnormally small in the case of certain non-aqueous solvents.

The choice of tetraethylammonium iodide as a "normal" electrolyte by Walden was based largely on solubility considerations. Apart from the difficult solubility, there would appear to be no particular reason for the selection of this in preference to an alkali metal iodide. The observations recorded in this paper indicate, however, that these are abnormally weak electrolytes when dissolved in certain liquid media, and any attempt to utilise them for comparison of the ionising powers of different solvents would therefore lead to discrepant results.

As to the cause of the difference between the ionisation of the iodides and that of the polyiodides, the various theories which have been put forward to account for the relative ionising powers of different solvents offer no explanation. This is necessarily the case in so far as such theories involve the consideration of the properties of the solvent alone. When, however, such large differences in ionisation are exhibited by closely related electrolytes in one and the same medium, it is clear that the character of the medium is of itself insufficient to account for the observed facts,

and some regard must be paid to the nature of the dissolved electrolyte.

In a recent paper (Turner, this vol., p. 880) evidence has been brought forward in favour of a connexion between electrical conductivity and molecular association. From a comparison of the molecular complexities and the electrical conductivities of a large number of halogen compounds, it appears that molecular association can only be exhibited by those substances which are electrically active. Salts, which in solvents of low dielectric constant are associated, exhibit electrolytic dissociation when dissolved in liquids of high dielectric constant. The formation of the polyiodides may be regarded as an association phenomenon, and the greater conductivity of these as compared with the simple iodides of the alkali metals is possibly a consequence of the association of iodine atoms which is involved in the formation of the complex polyiodides. Such association or formation of complexes would appear to be intimately bound up with the phenomenon of ionisation, for, generally speaking, the ionising solvents are those which show a pronounced tendency to form complex compounds with substances which are dissolved in them.

Physical Chemistry Laboratory,
The University, Leeds.

CLXXXII.—*Salts of* 3 : 5-*Dinitroquinol.*

By William Bayliss Shaw.

Although the salts of the mono-, di-, and tri-nitrophenols have attracted considerable attention during the last few years, the metallic derivatives of the nitrodihydroxybenzenes have remained practically unknown.

The author has prepared a considerable number of the alkali-metal salts of mono- and di-nitrohydroxybenzenes.

In the present communication those of 3:5-dinitroquinol are described, and the author hopes shortly to publish details of the corresponding derivatives of catechol and resorcinol.

Dinitroquinol was first obtained by Strecker (*Annalen*, 1861, **118**, 292) by the action of nitric acid on arbutin. Nietzki (*Ber.*, 1878, **11**, 469; *Annalen*, 1882, **215**, 142) obtained it by direct nitration of quinol diacetate. He prepared the neutral barium salt, but did not succeed in isolating any of the other salts owing to their great solubility in water.

It has, however, been found possible to obtain the alkali-metal salts of this substance in a very fair state of purity by the addition of an alcoholic solution of the metallic hydroxide to an ethereal solution of the nitro-compound. The salt is immediately precipitated, and is then collected and dried.

The analyses have been carried out by evaporating the salts with, first, a mixture of sulphuric and nitric acids, and then with sulphuric acid alone in a platinum crucible, the metal being thus determined as sulphate.

Experimental.

Preparation of 3:5-*Dinitroquinol.*

The method adopted was a modified form of Nietzki's process (*loc. cit.*).

One hundred grams of quinol were heated with 250 c.c. of acetic anhydride for about an hour in an oil-bath, the temperature being maintained between 130° and 140° (Hesse, *Annalen*, 1880, **200**, 244). The liquid was allowed to cool, and then slowly poured, with constant stirring, into a large volume of cold water, when quinol diacetate, being quite insoluble, separated out in colourless plates. The whole was kept for an hour or so in order to allow the excess of acetic anhydride to become hydrolysed, and the crystals were then collected and dried in the air. The yield was practically quantitative.

The quinol diacetate so obtained was directly nitrated according to Nietzki's directions (*loc. cit.*).

Nietzki's original method of hydrolysis consisted in dissolving the dinitroquinol diacetate in dilute sodium hydroxide, acidifying the violet solution so produced, and extracting the dinitroquinol with ether.

The following procedure was found to be much more expeditious. The dinitroquinol, washed as free as possible from nitric acid, was placed in an evaporating dish and covered with alcohol, a few c.c. of dilute hydrochloric acid being added to the mixture. On evaporating on the water-bath with occasional stirring, the acetyl groups were rapidly eliminated as acetic ester.

The process was repeated to ensure complete hydrolysis, although one evaporation was usually found to suffice.

The dinitroquinol obtained in this way was almost always pure yellow, but sometimes possessed a reddish tinge, probably due to the presence of some impurity. One recrystallisation from boiling water gave a substance which was practically pure.

The recrystallised dinitroquinol after being dried in a desiccator was pale yellow, and melted at 135°. It was employed for the preparation of the salts without further purification.

Preparation of the Salts.

One of the barium salts has already been described by Nietzki (*Annalen*, 1882, **215**, 144; *Ber.*, 1878, **11**, 470), who prepared it by the addition of baryta water to an aqueous solution of the nitro-compound.

He states that it crystallises in black needles, which resemble potassium permanganate. He found that it dissolved in an aqueous solution of the free nitro-compound with the formation of the yellow acid salt, which, however, he was not able to obtain in a pure form.

These two salts have now been prepared by slightly different methods in a state of purity.

Neutral Barium Salt, $C_6H_2(NO_2)_2O_2Ba,H_2O$.

Dinitroquinol was dissolved in alcohol, and baryta water was cautiously added until the liquid was very faintly alkaline. The dark-coloured precipitate was collected, washed well with alcohol and ether, and dried in a water-oven for several hours.

The substance when dry was a dark blue, crystalline solid, and was fairly explosive. It had no resemblance to the substance described by Nietzki.

Two separately prepared specimens were analysed:

(i) 0·1942 gave 0·1276 $BaSO_4$. Ba = 38·64.
(ii) 0·2227 „ 0·1472 $BaSO_4$. Ba = 38·86.

$C_6H_2O_6N_2Ba,H_2O$ requires Ba = 38·81 per cent.

The substance thus contains a molecule of water, and this it has not been found possible to remove, either by moderate heating or by keeping over sulphuric acid in a vacuum.

Nietzki does not give any particulars of his method of drying, but it is not easy to see how he obtained the salt in an anhydrous state.

Acid Barium Salt, $[HO\cdot C_6H_2(NO_2)_2\cdot O]_2Ba,2H_2O$.

This was prepared by boiling an aqueous solution of dinitroquinol with barium carbonate for about a quarter of an hour. The liquid was filtered hot, and, on cooling, deposited dark red crystals, which were collected, and dried in the water-oven.

Found: Ba = 24·15.

$C_{12}H_6O_{12}N_4Ba,2H_2O$ requires Ba = 23·99 per cent.

Neutral Lithium Salt, $C_6H_2(NO_2)_2(OLi)_2,H_2O$.

Dinitroquinol was dissolved in alcohol, and an aqueous solution of lithium hydroxide was added until the liquid was just alkaline. A little ether was then added, and the precipitate was collected, washed with alcohol and ether, and dried in the water-oven. The substance was dark violet.

Found: Li=6·00.

$C_6H_2O_6N_2Li_2,H_2O$ requires Li=6·09 per cent.

Acid Lithium Salt, $HO\cdot C_6H_2(NO_2)_2\cdot OLi$.

Dinitroquinol was dissolved in ether, and methyl-alcoholic lithium hydroxide added until the red liquid just began to acquire a violet colour. The red precipitate was collected, washed with ether, and dried.

Found: Li=3·36.

$C_6H_3O_6N_2Li$ requires Li=3·40 per cent.

Acid Sodium Salt, $C_6H_2(NO_2)_2(ONa)_2$.

Dinitroquinol was dissolved in the smallest possible quantity of alcohol, and largely diluted with ether. Dilute alcoholic sodium hydroxide was carefully added until the brown liquid showed a blue tinge. The precipitate was collected, washed with ether, and dried. It formed a brown solid.

Found: Na=10·68.

$C_6H_3O_6N_2Na$ requires Na=10·36 per cent.

Neutral Sodium Salt, $HO\cdot C_6H_2(NO_2)_2\cdot ONa$.

Dinitroquinol was dissolved, and treated as above, until a very slight excess of alkali was present. The precipitate was collected, washed, and dried as usual. The substance was a blue solid.

Found: Na=18·48.

$C_6H_2O_6N_2Na_2$ requires Na=18·85 per cent.

Acid Potassium Salt, $HO\cdot C_6H_2(NO_2)_2\cdot OK$.

Dinitroquinol was dissolved in alcohol, some ether was added, and then dilute alcoholic potassium hydroxide until the red liquid acquired a violet tinge. The precipitate was collected, washed, and dried. The substance was a brown solid.

Found: K=16·23.

$C_6H_3O_6N_2K$ requires K=16·39 per cent.

Neutral Potassium Salt, $C_6H_2(NO_2)_2(OK)_2,H_2O$.

The method of preparation was the same as in the case of the sodium salt, using alcoholic potassium hydroxide in place of alcoholic sodium hydroxide. The substance was dark violet.

Found: K = 26·22.

$C_6H_2O_6N_2K_2,H_2O$ requires K = 26·54 per cent.

Ammonium Salts.

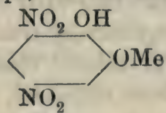
It has not been possible to obtain these in a state of purity owing to the readiness with which they lose ammonia.

3:5-*Dinitroquinol* 1-*Monomethyl Ether.*

This compound has been obtained by the following method.

Five grams of dinitroquinol were dissolved in half a litre of warm water, and the solution rendered alkaline with sodium hydroxide. A roughly estimated excess of methyl sulphate was then added, and the liquid maintained at about 60°, with continual shaking, until the violet solution became pale yellow. The liquid was then filtered hot, and allowed to cool, when the monomethyl ether separated in fine crystals, which did not need further purification.

Dinitroquinol monomethyl ether has already been described by Weselsky and Benedikt (*Monatsh.*, 1881, **2**, 370), who prepared it by the direct nitration of quinol monomethyl ether.

According to them it melts at 102°, but two carefully purified specimens prepared as above both melted at 97°. It is most probable that the methoxyl group occupies the meta-position with respect to the two nitro-groups, for the analogous dinitroguaiacol is known to have the formula  (Grimaux and Lefèvre, *Bull. Soc. chim.*, 1891, [iii], **5**, 418).

Salts of 3:5-*Dinitroquinol* 1-*Monomethyl Ether.*

Lithium Salt, $MeO{\cdot}C_6H_2(NO_2)_2{\cdot}OLi$.—The monomethyl ether was dissolved in warm chloroform, and a methyl-alcoholic solution of lithium hydroxide cautiously added until precipitation of the salt was complete. The precipitate was collected, washed with chloroform and ether, and dried.

Found: Li = 3·30.

$C_7H_5O_6N_2Li$ requires Li = 3·18 per cent.

Sodium Salt, $MeO{\cdot}C_6H_2(NO_2)_2{\cdot}ONa$.—The procedure was the

same as in the case of the lithium salt, alcoholic sodium hydroxide being substituted for methyl-alcoholic lithium hydroxide.

Found: Na = 10 5.

$C_7H_5O_6N_2Li$ requires Na = 9·74 per cent.

Potassium Salt, $MeO·C_6H_2(NO_2)_2·OK$.—This salt has been described by Weselsky and Benedikt (*loc. cit.*), who state that dinitroquinol monomethyl ether is soluble in warm potassium hydroxide, and that on cooling green crystals of the potassium salt are formed. No analysis or further particulars are given. This salt has been prepared in the following way.

The monomethyl ether was dissolved in ether, and dilute alcoholic potassium hydroxide added until precipitation was complete. The precipitate was collected, washed with ether, and dried in the water-oven:

0·1368 gave 0·0478 K_2SO_4. K = 15·66.

$C_7H_5O_6N_2K$ requires K = 15·47 per cent.

The salt is a bright crimson solid, which has no resemblance whatever to the substance described by Weselsky and Benedikt.

Ammonium Salt.—It has not been possible to prepare this salt in a state of purity, owing to the readiness with which it evolves ammonia.

The corresponding cæsium and rubidium salts of the above compounds have been prepared, but have not yet been analysed, owing to the difficulty of determining accurately the percentage of these metals in organic compounds.

The colours of the salts present some features of interest.

The neutral salts have in every case the darkest colours, the sodium and barium salts being blue, and the rest violet. The acid salts are dark red, and the ether salts bright red.

The colour deepens progressively from lithium to cæsium, but the barium salts are paler in colour than those of lithium. The ammonium salts have been obtained, although not in a state of purity, and appear to be intermediate in colour between those of barium and lithium. This is noteworthy since, crystallographically, ammonium is well known to stand near to rubidium.

In conclusion, I have to express my thanks to Professor E. von Meyer and Dr. W. König, of the Technische Hochschule, Dresden, for the kind interest they have taken in this work, and the many helpful suggestions they have made.

CLXXXIII.—2:2'-*Dibromodiphenyl and* 2:2'-*Dichlorodiphenyl.*

By JAMES JOHNSTON DOBBIE, JOHN JACOB FOX, and ARTHUR JOSIAH HOFFMEISTER GAUGE.

IN the course of an investigation having for its object the preparation of diphenylene (this vol., p. 683), it was necessary to obtain 2:2'-*dibromodiphenyl*, a substance hitherto unknown. Treatment of the tetrazo-derivative of 2:2'-diaminodiphenyl with cuprous bromide, as in the ordinary Sandmeyer reaction, suggested itself as a convenient method of preparation. This procedure ultimately proved successful, but unexpected difficulties arose in the first experiments, and very little dibromodiphenyl was formed. With the object of ascertaining the most suitable conditions for the reaction, the behaviour of cuprous bromide towards diphenyltetrazonium bromide under various conditions was investigated. Täuber had found that potassium sulphide reacted with diphenyltetrazonium chloride solutions, yielding carbazole (*Ber.*, 1893, **26**, 1703). This same substance had been obtained by v. Niementowski (*Ber.*, 1901, **36**, 3329), who made use of copper powder in an attempt to prepare dichlorodiphenyl. Mascarelli had also noticed that the main product of the reaction between diphenyltetrazonium chloride and potassium iodide was carbazole (*Gazzetta*, 1908, **38**, ii, 619), the di-iododiphenyl which was his aim being formed in small amount only. It is clear, therefore, that cuprous chloride and certain other reducing substances act on diphenyltetrazonium solutions mainly to produce the very stable substance carbazole.

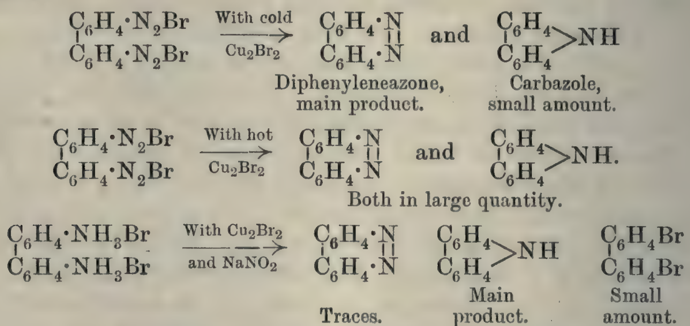
Cuprous bromide behaves in the same way as cuprous chloride, but at least two other products besides carbazole are formed simultaneously, namely, 2:2'-dibromodiphenyl and diphenyleneazone,

$$\begin{array}{l} C_6H_4\cdot N \\ | \qquad\; \| \\ C_6H_4\cdot N \end{array}.$$

When a solution of cuprous bromide dissolved in hydrobromic acid is poured into a cold solution of diphenyltetrazonium bromide, diphenyleneazone is the main product of the reaction, very little carbazole or dibromodiphenyl being formed. If, on the other hand, diphenyltetrazonium bromide is poured into a hot solution of cuprous bromide, carbazole is formed to a much greater extent, and the amount of diphenyleneazone is diminished. In this case also, very little dibromodiphenyl is produced. A much better yield of the latter substance with a little diphenyleneazone and a con-

siderable proportion of carbazole is obtained when 2:2′-diaminodiphenyl is dissolved in a hot solution of cuprous bromide in concentrated hydrobromic acid, and treated with sodium nitrite. The amount of 2:2′-dibromodiphenyl isolated from the product of the reaction rarely, however, exceeds 8 to 10 per cent. of the theoretical quantity.

In a study of the Sandmeyer reaction as applied to the formation of *o*-chlorotoluene, Erdmann (*Annalen*, 1893, **272**, 141) drew the conclusion that Sandmeyer's method of dissolving the base in a solution of the cuprous salt and halogen acid, and then diazotising, leads to a diminished yield of the required halogen derivative as compared with the yield obtained when the diazonium solution is poured into the solution of the cuprous salt. In the present instance the reverse is the case; Sandmeyer's method gives an appreciable amount of dibromodiphenyl, whereas Erdmann's produces mainly carbazole and diphenyleneazone, with only traces of dibromodiphenyl. The reactions which take place between diphenyltetrazonium bromide and cuprous bromide under the various conditions referred to may be represented by the following scheme:



In an attempt to prepare dibromodiphenyl by the action of alcohol on diphenyltetrazonium perbromide, only traces of dibromodiphenyl were obtained, carbazole being the main product of the reaction.

2:2′-Dibromodiphenyl can also be obtained from 2:2′-dibromo-4:4′-diaminodiphenyl by elimination of the amino-groups, both methods giving a product melting at 81°. As already shown in our previous paper, 2:2′-dibromodiphenyl reacts slowly with sodium, yielding diphenylene; mixed with methylene dibromide and acted on by sodium, it yields fluorene.

In order to complete the series of diortho-halogen derivatives of diphenyl, 2:2′-*dichlorodiphenyl* was prepared by a method similar to that used in the preparation of 2:2′-dibromodiphenyl. The yield of this substance was smaller than that of the correspond-

ing bromo-derivative, carbazole being again the main product. 2 : 2′-Dichlorodiphenyl crystallises from light petroleum in colourless prisms, melting at 59°. Both halogen derivatives are very stable towards oxidising agents, being scarcely, if at all, attacked, even by chromic acid mixture.

Experimental.

Formation of Diphenyleneazone.—2 : 2′ - Diaminodiphenyl was dissolved in excess of hydrobromic acid, and diluted with water until the solution contained approximately 3 per cent. of the base. The solution was cooled to 0°, and diazotised with sodium nitrite. To the tetrazonium solution so formed, cuprous bromide, dissolved in hydrobromic acid (40 grams of Cu_2Br_2 to 50 c.c. of acid, D 1·49), was slowly added with stirring, the solution being kept cool by means of ice. Each addition of cuprous bromide was followed by a vigorous evolution of gas and formation of a bluish-black mass enclosing nitric oxide. The products of the reaction were heated on a water-bath for an hour, and the liquid then filtered from the solid matter (A). The filtrate was evaporated to small volume, and on treatment with excess of ammonia a large amount of almost pure diphenyleneazone was precipitated. The solid (A) was boiled with 15 per cent. hydrochloric acid, the acid liquid filtered from undissolved solid matter (B), and the filtrate treated with excess of ammonia, which precipitated a further quantity of slightly impure diphenyleneazone. After one crystallisation from alcohol, the diphenyleneazone was obtained pure in the form of long, greenish-yellow prisms, melting at 155°. The yield was good, 11 grams of pure material being obtained from 20 grams of 2 : 2′-diaminodiphenyl. The identity of this substance with the diphenyleneazone obtained by Täuber by the action of sodium amalgam on 2 : 2′-dinitrodiphenyl (*Ber.*, 1891, **24**, 3081), and by Ullmann and Dieterle from diphenyleneazone oxide (*Ber.*, 1904, **37**, 23), was proved by the melting point and by analysis of the base (Found, N = 15·7. Calc., N = 15·6 per cent.) and of the platinum salt. (Found, Pt = 25·1. Calc., Pt = 25·0 per cent.)

It is noteworthy that the formation of diphenyleneazone by the above process is accompanied by evolution of nitric oxide.

The solid (B) was found to contain carbazole, which was extracted by successive treatment with alcohol, ether, benzene, and carbon tetrachloride. These solutions were boiled with animal charcoal, and concentrated, when crystals were deposited, from which pure carbazole was ultimately obtained. The first crops of carbazole crystals were mixed with a very small quantity of dibromodiphenyl.

Attempts to increase the yields of dibromodiphenyl were next made by modifying the method described above in various directions. The diphenyltetrazonium bromide solution was poured into a hot solution of cuprous bromide dissolved in hydrobromic acid. The black, tarry solid which formed yielded a fair amount of carbazole and of diphenyleneazone, but only traces of dibromodiphenyl. By this method the amount of diphenyleneazone was diminished, and that of the carbazole increased.

Preparation of 2 : 2′-Dibromodiphenyl.—When 2:2′-diaminodiphenyl hydrobromide is diazotised in the presence of cuprous bromide, dibromodiphenyl is formed, together with other products. Thirty-six grams of cuprous bromide were dissolved in 90 c.c. of hydrobromic acid (D 1·49), and 20 grams of 2:2′-diaminodiphenyl added. The liquid was heated on a water-bath, and small quantities of hot water added from time to time until all the solid was dissolved. Sixteen grams of sodium nitrite in 50 c.c. of water were added to the hot solution of the base drop by drop, with vigorous stirring after the addition of each drop, the heating being continued during the addition of the nitrite solution. When all the nitrite had been added, the liquid was heated on a water-bath for an hour, cooled, and diluted with water. The dark soft solid which separated was collected, washed with water, and digested with ether several times. A considerable amount of solid matter containing carbazole remained undissolved in the ether. The undissolved matter also contained some copper compound, but this was not further investigated. A very small amount of diphenyleneazone was obtained from the aqueous filtrate from the soft solid. The ethereal solution, which contained almost all the dibromodiphenyl, was boiled with animal charcoal, filtered, and evaporated to a syrupy consistency. The syrupy residue was distilled in a current of steam, in which the dibromodiphenyl, together with a little carbazole, passed over. This method of separation is slow, but, so far, is the only one by which we have been able to obtain dibromodiphenyl free from coloured impurities. The distillate was extracted with ether, and the crystalline residue obtained by evaporation of the ethereal solution, dissolved in light petroleum (boiling below 60°), and allowed to crystallise. A small quantity of carbazole first separated, and was removed by filtration. Dibromodiphenyl crystallised from the filtrate in long, hard, colourless prisms or in feathery tufts of needles, which melted at 81° after recrystallisation from 90 per cent. alcohol. The yield is about 15 per cent. of the weight of the base employed.

2:2′-*Dibromodiphenyl* is readily soluble in the usual organic solvents. It is very stable towards oxidising agents; after heating

with a mixture of chromic acid and diluted sulphuric acid for five hours practically the whole of the substance was recovered unchanged. Advantage may be taken of this fact to remove traces of impurities:

0·1346 gave 0·2262 CO_2 and 0·0323 H_2O. C=45·9; H=2·65.
0·1226 „ 0·1482 AgBr. Br=51·4.
$C_{12}H_8Br_2$ requires C=46·2; H=2·6; Br=51·3 per cent.

The constitution of dibromodiphenyl follows from its preparation from 2 : 2′-diaminodiphenyl.

2 : 2′-Dibromodiphenyl can also be prepared from 2 : 2′-dibromo-4 : 4′-diaminodiphenyl (*mm′*-dibromobenzidine), a substance which was obtained by Gabriel from *m*-bromonitrobenzene (*Ber.*, 1876, **9**, 1405). For the preparation of dibromodiphenyl, the hydrochloride which is obtained from *mm′*-dibromohydrazobenzene may be used directly after drying. The amino-groups can be removed by means of ethyl nitrite and alcohol in the usual way. The resulting alcoholic solution is evaporated to dryness, and the residue distilled in steam, whereby an impure dibromodiphenyl is obtained. After purification, the substance prepared in this way melted at 81°, and no alteration in the melting point was observed when it was mixed with the dibromodiphenyl prepared from 2 : 2′-diaminodiphenyl. As regards yield, the preparation from *mm′*-dibromobenzidine offers no advantage over the first method, and the final product requires several recrystallisations involving considerable loss of material before it is obtained quite pure.

An attempt to prepare 2 : 2′-dibromodiphenyl through a perbromide was made. 2 : 2′-Diaminodiphenyl was diazotised, and to the tetrazo-solution a mixture of bromine in hydrobromic acid was added. A bulky, yellow precipitate of the perbromide formed at once. This was collected, and boiled with absolute alcohol, the solution changing in colour through green and blue to brown. After removal of the alcohol a fair amount of diphenyleneazone was obtained, but only traces of halogen derivative.

Preparation of 2 : 2′-Dichlorodiphenyl.—2 : 2′-Diaminodiphenyl was dissolved in hydrochloric acid containing the calculated quantity of cuprous chloride. The solution was then heated, and treated with sodium nitrite, as in the preparation of 2 : 2′-dibromodiphenyl. The subsequent treatment of the soft, black solid was also similar. A large amount of carbazole was isolated from the reaction products, and a small quantity of dichlorodiphenyl was found in the ethereal solutions. After distillation in a current of steam a mixture of dichlorodiphenyl with a little carbazole was obtained, from which the pure dichlorodiphenyl was isolated by recrystallisation from light petroleum, in which carbazole is but sparingly soluble.

2 : 2′-*Dichlorodiphenyl* crystallises from light petroleum in nodular masses of colourless prisms, melting at 59°. It dissolves in the usual organic solvents, and is stable towards oxidising agents:

0·1134 gave 0·1428 AgCl. Cl = 31·2.

$C_{12}H_8Cl_2$ requires Cl = 31·8 per cent.

An interesting synthesis of fluorene was effected by the action of sodium on a mixture of 2 : 2′-dibromodiphenyl and excess of methylene dibromide dissolved in ether. The crystalline residue remaining after evaporating off the ether contained unchanged dibromodiphenyl, which was removed by recrystallisation from alcohol and light petroleum. After recrystallisation several times from these solvents a small amount of almost pure fluorene was obtained, melting at 115°. The substance was further identified by the preparation of the characteristic brown picrate, melting at 80°.

GOVERNMENT LABORATORY,
LONDON.

CLXXXIV.—*The β-Chlorocinnamic Acids.*

By THOMAS CAMPBELL JAMES.

THE β-chlorocinnamic acids have been previously studied by W. H. Perkin, jun. (Trans., 1885, **47**, 256), by Michael and Pendleton (*J. pr. Chem.*, 1889, [ii], **40**, 65), and by Mulliken (*Diss.*, Leipzig, 1890). Perkin found that when phosphorus pentachloride was added to ethyl benzoylacetate in phosphoryl chloride solution, a chlorocinnamic acid, melting at 142°, was obtained, which was supposed by him to be identical with the α-chlorocinnamic acid, melting at 138°, previously prepared by Plochl (*Ber.*, 1882, **15**, 1945).

The application of the theory of stereoisomerism to unsaturated compounds indicated the possible existence of two β-chlorocinnamic acids, $C_6H_5 \cdot CCl{:}CH \cdot CO_2H$, as well as two α-acids,

$$C_6H_5 \cdot CH{:}CCl \cdot CO_2H.$$

The former were prepared by Michael and Pendleton (*loc. cit.*) by the addition of hydrogen chloride to phenylpropiolic acid in acetic acid solution. They were separated by taking advantage of the great difference of solubility of their potassium salts in absolute alcohol. The acid obtained from the readily soluble salt melted at 132·5°, and was called β-chlorocinnamic acid, the other melting at 142°, β-chloro*allo*cinnamic acid.

Mulliken showed that phenylpropiolic acid combines with hydrogen chloride when it is heated with the fuming aqueous acid at 80—90° for three hours. By examining the action of heat on the two isomerides, he found that the acid melting at 142° was the more stable, and should therefore be called β-chlorocinnamic acid, the compound of lower melting point being the *allo*-acid.

In the present investigation the methods of preparation mentioned above have been examined, and the proportion in which the two isomerides are formed determined in each case. It has been found that the method of separation by means of barium salts applied in the case of the α- and β-bromocinnamic acids (Sudborough and Thompson, Trans., 1903, **83**, 666, 1153) and the α-chlorocinnamic acids (Sudborough and James, Trans., 1906, **89**, 105) is applicable in this case also. The action of sunlight on the two isomerides and the rates of elimination of hydrogen chloride have been examined, the results of these experiments taken in conjunction with the esterification constants (Sudborough and Roberts, Trans., 1905, **87**, 1849) proving definitely that the acid melting at 132·5° is the *allo*-compound. Various derivatives of the acids have also been prepared.

Experimental.

Separation of the β-Chlorocinnamic Acids.

Two grams of each acid were mixed and dissolved in water with the addition of aqueous ammonia, the total volume being 40 c.c. After neutralising the excess of ammonia with hydrochloric acid, 20 c.c. of a cold saturated solution of barium chloride were added, and the mixture allowed to remain for two hours. The precipitated barium salt was collected, and washed three times with small quantities of dilute barium chloride solution, after which it was treated with dilute hydrochloric acid. The filtrate containing the soluble barium salt was treated with concentrated hydrochloric acid, and the acids precipitated in each case were washed with dilute acid, dried, and weighed.

The sparingly soluble barium salt gave 2·06 grams of acid, which after recrystallisation melted at 142°. The soluble salt gave 1·92 grams of acid, melting at 131°. Total yield, 3·98 grams. The separation is therefore complete to within 4 per cent.

Preparation of β-Chlorocinnamic Acids.

Method 1. *By the addition of hydrogen chloride in aqueous solution to phenylpropiolic acid.*—Mulliken (*loc. cit.*) established the fact that at temperatures below 80° addition of hydrogen chloride to phenylpropiolic acid takes place only very slowly.

Between 80° and 90° addition is complete in three hours, but considerable decomposition of the products takes place with the formation of acetophenone. No yields are mentioned, but the proportion of β-chloro-acid to its *allo*-isomeride is given at 61 : 39.

A series of experiments has confirmed Mulliken's results with regard to the conditions under which addition takes place. The total yield of β-chloro-acids is only about 40 per cent. of theory, of which rather more than one-half consists of the *allo*-isomeride.

A weighed amount of phenylpropiolic acid was placed in a bomb tube, and treated with sufficient hydrogen chloride solution, saturated at 0°, to cover it. After sealing, the tube was heated in a water-bath kept at 80—90° for three hours. The product, which contained much oil, was washed with water, extracted with dilute alkali, and the solution, after neutralising, treated with barium chloride solution as described above. The results are given in the following table:

Experiment.	Phenylpropiolic acid. Grams.	Temperature.	β-Chloro-acid. Grams.	Yield per cent.	*allo*-Acid. Grams.	Yield per cent.	Total yield per cent.
1.	4	80—90°	0·80	16	0·95	19	35
2.	4	80—90	0·85	17	1·25	25	42
3.	6	83°	1·50	20	1·60	21	41
		Average yields.........		18		22	40

Method 2. *By the addition of hydrogen chloride to phenylpropiolic acid in acetic acid solution at the ordinary temperature.*—Michael and Pendleton (*loc. cit.*) state that the addition of hydrogen chloride to phenylpropiolic acid in acetic acid solution produces the two isomerides, which after precipitating by adding to excess of water were separated by taking advantage of the difference of solubility of the potassium salts in absolute alcohol.

Ten grams of phenylpropiolic acid were dissolved in 50 grams of glacial acetic acid, and dry hydrogen chloride passed in until the solution was saturated at 0°. The mixture was kept in a sealed bottle in the dark at the ordinary temperature. Preliminary experiments showed that it required six weeks to attain complete addition under these conditions.

Experiment 1.—After remaining for six weeks the mixture was poured into excess of water, the precipitate collected, dried, and weighed. Weight = 10·1 grams (theory, 12·5 grams).

Experiment 2.—After six weeks the mixture was poured into an evaporating dish, and the solvent allowed to evaporate off in a fume-cupboard in a dark room. Weight of product = 11·0 grams.

Experiment 3.—It was found that by heating the mixture to 50—60°, addition takes place in eight hours, little oil-formation

occurring. Five grams of acid dissolved in 50 grams of acetic acid under these conditions yielded 4·0 grams of mixed acids.

The products in each case were separated by the barium salt method with the following results:

Experiment.	Weight of crude mixture. Grams.	β-Chloro-acid. Grams.	Yield per cent.	β-Chloro-*allo*-acid. Grams.	Yield per cent.
1.	10·1	5·0	40·0	4·4	35·2
2.	11·0	5·1	41·0	5·6	44·8
3.	4·0	1·6	25·6	1·8	28·8

The products possessed the correct melting points after one recrystallisation from alcohol and water. The numbers indicate that in each case approximately equal amounts of the two isomerides are obtained.

Method 3. *By the action of phosphorus pentachloride on the esters of benzoylacetic acid.*—Perkin in his investigation of benzoylacetic acid and its derivatives (*loc. cit.*) obtained a chlorocinnamic acid, melting at 142°, by the action of phosphorus pentachloride on the ethyl ester. Mulliken repeated the experiment, and identified the acid with the β-chlorocinnamic acid obtained by method 1. He also showed that the oily by-product of the reaction contains acetophenone.

A series of experiments carried out with the methyl and ethyl esters shows that both acids are obtained during the reaction. The method of procedure was based on that of Perkin.

Ten grams of the ester were dissolved in 25 grams of phosphoryl chloride (or phosphorus trichloride), and the solution added gradually to 25 grams of phosphorus pentachloride in a distilling flask. When the evolution of hydrogen chloride had ceased, the flask was heated in a water-bath until the solid pentachloride had disappeared. The phosphoryl chloride was then distilled off under diminished pressure, and the residue, after cooling, poured into water. The product, which contained much oil, was dissolved in ether, and shaken several times with small amounts of dilute ammonia solution to extract the acids. The aqueous extracts, after neutralising with hydrochloric acid, were treated with barium chloride solution and worked up in the usual manner.

The ethereal solution, after extracting the acids, was dried, and the ether distilled off, leaving a yellow oil. That derived from the experiments with the ethyl ester was distilled. The first fraction (25 per cent.), collected at 200—220°, contained only traces of chlorine, gave a phenylhydrazone, melting at 105°, and was therefore acetophenone. The second fraction (50 per cent.), collected at 240—275°, boiled chiefly at 260—265° (uncorr.). It contained

15·5 per cent. of chlorine, and is the ester of an unsaturated acid, probably β-chloro*allo*cinnamic acid. The remaining portion charred and decomposed on heating further.

Experiment 1.—Ten grams of ethyl benzoylacetate were dissolved in 25 grams of phosphoryl chloride, and added gradually to 25 grams of phosphorus pentachloride. After separation there were obtained:

β-Chlorocinnamic acid	4·60 grams	or	51·0 per cent.
β-Chloro*allo*cinnamic acid..	1·50 ,,	,,	16·4 ,, ,,
Oil	2·0 ,,		
Total yield of acids.........			67·4 ,, ,,

Experiment 2.—Same as No. 1.

β-Chloro-acid..................	3·95 grams	or	44·0 per cent.
β-Chloro*allo*-acid	1·75 ,,	,,	19·4 ,, ,,
Oil	3·0 ,,		
Total yield of acids............			63·4 ,, ,,

Experiment 3.—Solvent, phosphorus trichloride; otherwise as in Nos. 1 and 2.

Crude product	7·20 grams		
β-Chloro-acid..................	4·65 ,,	or	51·6 per cent.
β-Chloro*allo*-acid	1·90 ,,	,,	21·1 ,, ,,
Total yield of acids............			72·7 ,, ,,

Experiment 4.—As in No. 3, but the benzoylacetic ester was distilled immediately before the experiment.

β-Chloro-acid..................	3·90 grams	or	43·3 per cent.
β-Chloro*allo*-acid	2·10 ,,	,,	23·3 ,, ,,
Total yield of acids			66·6 ,, ,,
Average yield of β-chlorocinnamic acid (4 experiments).			47·5 ,, ,,
,, ,, β-Chloro*allo*cinnamic acid			20·0 ,, ,,

An experiment conducted with the methyl ester gave an improved yield of β-chlorocinnamic acid, with an increased proportion of the *allo*-acid.

Experiment 5.—Ten grams of methyl benzoylacetate in 25 grams of phosphorus trichloride added to 25 grams of phosphorus pentachloride.

Crude product	9·2 grams		
β-Chlorocinnamic acid......	4·10 ,,	or	42·0 per cent.
β-Chloro*allo*cinnamic acid..	3·75 ,,	,,	38·0 ,, ,,
Oil	1·0 ,,		
Total yield of acids...........			80·0 ,, ,,

*Transformation of β-Chloro*allo*cinnamic Acid into its Isomeride.*

Mulliken has shown that the acid melting at 132·5° is largely transformed into the acid of higher melting point when kept at a

temperature of 150° for five hours. A similar transformation occurs at the ordinary temperature under the influence of sunlight.

One gram of each acid was exposed to sunlight during two months. At the end of this time the point of fusion of the acid of higher melting point was unchanged, but that of the other fell to 120°. On separation by means of barium salts the latter gave 0·2 gram of β-chlorocinnamic acid, melting at 142°.

Action of Potassium Hydroxide on β-Chlorocinnamic Acids.

By remaining in contact with aqueous alkalis both acids lose hydrogen chloride and yield phenylpropiolic acid.

Experiment 1.—Two grams of β-chlorocinnamic acid were warmed with 2·5 mols. of aqueous potassium hydroxide solution (10 per cent.) on a water-bath for two hours. On acidifying, 1·55 grams of phenylpropiolic acid (m. p. 136°) were obtained. Theory, 1·60 grams.

Experiment 2.—A similar experiment was carried out with β-chloro*allo*cinnamic acid, the mixture being warmed for six hours.

1·35 Grams of phenylpropiolic acid were obtained, and the odour of phenylacetylene was detected, indicating partial decomposition of the carboxylic grouping.

The rate of elimination of hydrogen chloride by potassium hydroxide has been determined kinetically.

β-Chlorocinnamic Acid.—1/100 Gram-equivalent of the acid was dissolved in 2 equivalents of *N*/10-potassium hydroxide solution. Twenty-five c.c. of the resulting solution were titrated at intervals with standard sulphuric acid.

Temperature of bath 15°. Strength of acid used for titration, 0·05708*N*.

Time in hours.	C.c. acid required.	x.	$k = 1/t \cdot \frac{x}{a(a-x)}$.
0·0	21·90	—	—
42·5	20·50	1·40	0·0000734
113·5	18·60	3·30	0·0000713
185·5	16·95	4·95	0·0000702
305 5	14·80	7·10	0·0000717
324·0	13·60	8·30	0·0000726
		Mean........................	0·00007184

Calculated for normal solution $k = 0·0315$.

*β-Chloro*allo*cinnamic Acid.*—Three grams of the acid were dissolved in 2 equivalents of *N*/5-potassium hydroxide. Twenty c.c. of the resulting solution were titrated at intervals with standard sulphuric acid.

Temperature of bath 15°. Strength of acid used for titration, 0·1042*N*.

Time in hours.	C.c. acid required.	x.	$k=1/t\frac{x}{a(a-x)}$.
0	19·76	—	—
24	19·36	0·40	—
144	18·85	0·91	0·0000169
336	17·95	1·81	0·0000152
432	17·60	2·16	0·0000144
504	17·30	2·46	0·0000143
768	16·60	3·16	0·0000125
	Mean...........................		0·0000147

Calculated for normal solution k = 0·00282.

From these values it is seen that β-chlorocinnamic acid (m. p. 142°) loses hydrogen chloride about eleven times as rapidly as β-chloro*allo*cinnamic acid (m. p. 132°).

Derivatives of the β-Chlorocinnamic Acids.

β-Chlorocinnamic Acid.

Ethyl Ester.—Eight grams of acid were dissolved in 40 grams of absolute alcohol, and dry hydrogen chloride passed in until a 10 per cent. solution was obtained. The solution was boiled for six hours, and then worked up in the usual manner. Yield of ester, 6 grams. Boiling point, 293° (corr.):

0·2149 gave 0·1478 AgCl. Cl=17·01.

$C_{11}H_{11}O_2Cl$ requires Cl=16·85 per cent.

Amide.—Colourless, crystalline needles, melting at 118°:

0·2002 required 11·17 c.c. *N*/10-$AgNO_3$. Cl=19·78.

C_9H_8ONCl requires Cl=19·50 per cent.

Anilide.—Colourless, crystalline needles, melting at 128°:

0·2180 required 8·55 c.c. *N*/10-$AgNO_3$. Cl=13·90.

$C_{15}H_{12}ONCl$ requires Cl=13·77 per cent.

p-*Toluidide.*—Crystalline needles, melting at 122·5°:

0·2050 required 7·67 c.c. *N*/10-$AgNO_3$. Cl=13·24.

$C_{16}H_{14}ONCl$ requires Cl=13·06 per cent.

*β-Chloro*allo*cinnamic Acid.*

Ethyl Ester.—Five grams of the acid were dissolved in 25 grams of absolute alcohol, and dry hydrogen chloride passed in until a 10 per cent. solution was obtained. After boiling on a water-bath for nine hours, the ester was separated in the usual manner. Yield, 4·0 grams. The ester boils at 265° (corr.), with slight decomposition:

0·2022 gave 0·1408 AgCl. Cl = 17·22.

$C_{11}H_{11}O_2Cl$ requires Cl = 16·85 per cent.

The acid chloride was prepared by adding the theoretical amount of phosphorus pentachloride to a chloroform solution of the acid, warming in a water-bath until the action was completed, and then distilling off the solvent and the oxychloride under diminished pressure. This was not analysed, but was converted into the following derivatives in the usual manner.

Amide.—Crystalline needles, melting at 76°:

0·2080 required 11·38 c.c. *N*/10-$AgNO_3$. Cl = 19·38.

0·2690 gave 17·6 c.c. N_2 at 15° and 777 mm. N = 7·90.

C_9H_8ONCl requires Cl = 19·50; N = 7·77 per cent.

Anilide.—Colourless, crystalline needles, melting at 134·5°:

0·1324 required 5·16 c.c. *N*/10-$AgNO_3$. Cl = 13·81.

$C_{15}H_{12}ONCl$ requires Cl = 13·77 per cent.

p-*Toluidide.*—Crystalline needles, melting at 142°:

0·2014 required 7·63 c.c. *N*/10-$AgNO_3$. Cl = 13·43.

$C_{16}H_{14}ONCl$ requires Cl = 13·06 per cent.

The estimation of chlorine was carried out in each case by Stepanoff's method (*Ber.*, 1906, **39**, 4056).

In conclusion, I desire to express my thanks to Professor J. J. Sudborough for his interest in the work, and to Mr. Idwal Morgan, B.Sc., for assistance in the preparation and analysis of certain of the compounds.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
ABERYSTWYTH.

CLXXXV.—*The Condensation of Crotonaldehyde.*

By IDA SMEDLEY (Beit Memorial Research Fellow).

THE readiness with which aldehydes undergo the aldol condensation in dilute alkaline solutions led Nencki and, later, Magnus Levy to suggest that in the synthesis of fatty acids from carbohydrates which is believed to occur in the animal body, the aldol reaction may take part. Since acetaldehyde may be obtained as a decomposition product of carbohydrates, the production of butyric acid may be assumed to occur by the oxidation and reduction of the aldol formed on condensing two molecules of acetaldehyde. When, however, this hypothesis is applied to explain the formation of the

higher fatty acids, it is no longer in harmony with our knowledge of the aldol reaction; Lieben and his students investigated a large number of aldehyde condensations, and showed that when the higher fatty aldehydes condense, the resulting aldehydes contain branched carbon chains; the hydrogen atom of a CH group was found to react more readily than that of a CH_2 group, the methylene hydrogen more readily than that of a methyl group (*Monatsh.*, 1883, **4**, 10; 1901, **22**, 289). Thus, the interaction of propaldehyde and acetaldehyde leads to the production of tiglic aldehyde,* and not of the normal chain aldehyde required for the application of this reaction to the synthesis of the fatty acids:

$$CH_3{\cdot}CHO + CH_3{\cdot}CH_2{\cdot}CHO = CH_3{\cdot}CH{:}C(CH_3){\cdot}CHO.$$

The formation of the unsaturated aldehyde or of the intermediate hydroxy-compound was found to depend on the strength of the alkaline condensing agent used. Previously, Schmidt had described the reaction between furfuraldehyde and propaldehyde as taking place between the furfuraldehyde group and the β-carbon atom of the propaldehyde; no evidence for this was, however, given, and from Lieben's work it appears improbable that the reaction can take place in this direction (Schmidt, *Ber.*, 1881, **18**, 574).

The condensation of aldol was studied by Raper (Trans., 1907, **91**, 1831), who obtained the remarkable result that *n*-octoic acid was produced by reducing with hydriodic acid and phosphorus the acid formed by oxidation of the condensation product of aldol. This involved the condensation of the aldehyde group with the hydrogen attached to a γ-carbon atom. During the condensation a molecule of water was lost, but evidence was lacking as to how this had been eliminated.

The important modification brought about in the aldol reaction by the introduction of a β-hydroxyl group made it desirable that the influence of other groups should be determined, and the effect of the ethenoid linking on the aldol condensation has, therefore, been examined, crotonaldehyde being chosen for investigation.

The condensation of crotonaldehyde under the influence of acid condensing agents has been investigated by Delépine (*Compt. rend.*, 1910, **150**, 394), who obtained a bimolecular product, $C_8H_{12}O_2$, boiling at 86—87°/18 mm., to which he attributed a cyclic formula.

The author has now investigated the action of solutions of potassium acetate, potassium carbonate, potassium hydroxide, sodium hydroxide, and guanidine carbonate in varying concentrations on crotonaldehyde; the most favourable conditions appeared

* Tiglic acid, although not known as a constituent of fats, occurs plentifully in nature as a constituent of croton oil.

to be obtained by dissolving crotonaldehyde in ten times its volume of *N*/10-potassium carbonate, and leaving the solution for three days at the ordinary temperature. With solutions weaker than *N*/20 and stronger than *N*/5, the reaction proceeded more slowly; at 0° solutions of crotonaldehyde in *N*/10-potassium carbonate underwent very little change in three days. In each case the amount of potassium carbonate was found to be practically unchanged at the end of the experiment. If, however, dilute solutions of the alkali hydroxides were used, a considerable proportion was neutralised during the course of the experiment, the condensation product apparently undergoing the Cannizzaro reaction (compare Lieben, *loc. cit.*). The soluble condensation product decomposed when it was distilled under a pressure of 10—15 mm.; no characteristic crystalline derivatives were obtained from it. By the action of silver oxide an unsaturated hydroxy-acid was obtained, having the formula $C_8H_{12}O_3$, which absorbed hydrogen in the presence of finely divided platinum; on treating with hydriodic acid and phosphorus it was converted into octoic acid. The difficulties attending the purification and identification of the condensation product are such that it is not possible to say with any degree of certainty whether it is a single substance or a mixture of isomerides. The proportion of the normal eight-carbon chain present in the condensation product is, therefore, uncertain; the detection of *n*-octoic acid in the reduction product establishes, however, that a compound containing a straight chain of eight-carbon atoms is formed in the reaction.

Raper's work on the condensation of aldol was repeated, and his final reduction product prepared for comparison with the specimen of octoic acid obtained from the crotonaldehyde condensation product. The yields were in both cases very small, that from the aldol product being rather the better; in each case from 40 grams of the barium salt of the unreduced acid about 0·1 gram of the pure amide was obtained, melting at 103—104°; the melting point was unchanged on mixing together, and each was separately mixed with octoamide prepared from Kahlbaum's pure octoic acid, the melting point of each mixture being unaltered (103—104°). When mixed with the amide of ethylhexoic acid (Raper, *loc. cit.*), which melts at 101—102°, the melting point was lowered to 95°. There are considerable differences in the melting points assigned by different observers to octoamide; they range from 99° to 110°; Raper gives 105—106°. After two recrystallisations from water and one from petroleum, the three specimens examined by the author melted at 103—104°. The amide of 1-methyl*cyclo*hexane-2-carboxylic acid (m. p. 181°), which might conceivably be formed

by the conversion of the straight-chain compound into a cyclic compound, as in the case of the olefinic terpenes, was not detected.

The dimethyl*cyclo*pentanecarboxylic acid which might be formed from the branched-chain product is not known, but the identification of the octoic acid seemed convincing. Analysis of the amide obtained partly by the reduction of the crotonaldehyde condensation product and partly from the aldol product gave results agreeing with those required for octoamide.

Since in the condensation of aldol a molecule of water is eliminated, it is possible that this reaction really consists of the condensation of a molecule of aldol with one of crotonaldehyde:

$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO + CH_3{\cdot}CH{:}CH{\cdot}CHO = CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH{:}CH{\cdot}CHO.$$

In the case of crotonaldehyde, no water appears to be lost during the condensation, and it may be supposed, therefore, that the reaction proceeds as follows:

$$CH_3{\cdot}CH{:}CH{\cdot}CHO + CH_3{\cdot}CH{:}CH{\cdot}CHO = CH_3{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}CH{:}CH{\cdot}CHO.$$

It is interesting to compare this structure with that of the widely-distributed group of olefinic terpene compounds, for example, with citral:

Crotonaldehyde condensation product ...	$CH_3{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}CH{:}CH{\cdot}CHO$
Citral	$(CH_3)_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}C(CH_3){:}CH{\cdot}CHO$

The relative position of the double bonds is the same as in the crotonaldehyde condensation product, and a consideration of the position of the methyl groups suggests that the terpene chain may be produced by an aldol condensation of a methyl derivative of crotonaldehyde similar to that just described:

$$(CH_3)_2C{:}CH{\cdot}CHO + (CH_3)_2C{:}CH{\cdot}CHO = (CH_3)_2C{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}C(CH_3){:}CH{\cdot}CHO.$$

Such a product differs from citral only in the substitution of a hydroxyl group for a hydrogen atom. The methyl derivative of crotonaldehyde, $(CH_3)_2C{:}CH{\cdot}CHO$, required for this condensation has not yet been prepared; it is possible that in the organism acetone and aldehyde may be condensed so as to produce this compound:

$$(CH_3)_2CO + CH_3{\cdot}CHO = (CH_3)_2C{:}CH{\cdot}CHO + H_2O,$$

although in the laboratory such a synthesis has not yet been effected.

Raper's synthesis of a normal eight-carbon-chain compound and the synthesis, now described, of the same chain from crotonaldehyde suggest that it may be possible by the introduction of ethenoid linkings or hydroxyl groups so to modify the reactivity of the

compound that the carbonyl group of the higher aldehyde will react with the methyl group of acetaldehyde, and give the normal carbon chains required for the formation of fatty acids.

In the only other case of aldol condensation described in which crotonaldehyde takes part it is perhaps significant that it is the crotonaldehyde carbonyl group that reacts, for the condensation of crotonaldehyde and *iso*butyraldehyde is described as taking place as follows (Plattensteiner, *Monatsh.*, 1901, **22**, 14):

$$CH_3\cdot CH\colon CH\cdot CHO + (CH_3)_2CH\cdot CHO = \\ CH_3\cdot CH\colon CH\cdot CH(OH)\cdot C(CH_3)_2\cdot CHO.$$

The author is at present engaged in investigating further the condensation of unsaturated aldehydes.

Experimental.

Twenty grams of crotonaldehyde prepared by Delépine's method (*Compt. rend.*, 1908, **147**, 1316) were dissolved in 200 c.c. of $N/10$-potassium carbonate, and the solution left at the ordinary temperature for three days. After about one hour the solution had become yellow. A small amount of a yellow, insoluble oil separated, and at the end of the third day the odour of crotonaldehyde was much fainter. The solution was diluted with 500 c.c. of water, filtered, and neutralised with hydrochloric acid. Excess of barium carbonate was added, and the liquid distilled in a current of steam for from two to three hours. The filtered solution was then concentrated under diminished pressure, and the residue extracted with ether. The ethereal solution, after being dried and evaporated, left a viscous oil, which was placed in a vacuum desiccator over concentrated sulphuric acid for some days:

0·1882 gave 0·4568 CO_2 and 0·1484 H_2O. C = 66·21; H = 8·77.

$C_8H_{12}O_2$ requires C = 68·57; H = 8·57 per cent.

The liquid decomposed when distilled under a pressure of 15 mm., and no satisfactory method of further purifying it was found. It reduced Fehling's solution, and deposited a silver mirror on warming with ammoniacal silver nitrate.

In preparing the condensation product for oxidation and subsequent reduction with hydriodic acid, the steam distillation was omitted, and the solution evaporated at about 50°. The amount of the product thus obtained was considerably increased, and the odour of crotonaldehyde could not be detected in it; yet considerable quantities of butyric acid were obtained in the reduction.

Oxidation with Silver Oxide:—A solution of 10 grams of the condensation product was added to 40 grams of silver oxide (freshly precipitated and washed by decantation), and 200 c.c. of

N/2-barium hydroxide gradually added, the solution being kept cool. After remaining overnight, carbon dioxide was passed into the filtered solution to remove the excess of barium hydroxide. The filtered solution was evaporated to dryness under diminished pressure, extracted with alcohol, the barium salt precipitated by dry ether, and dried at 100°:

0·1858 gave 0·0970 $BaSO_4$. Ba = 30·68.

$(C_8H_{11}O_3)_2Ba$ requires Ba = 30·65 per cent.

Reduction with Sodium Amalgam:—Reduction with sodium amalgam produced a viscous liquid, which was not satisfactorily characterised. It was dried for eight days in a vacuum desiccator:

0·1065 gave 0·2590 CO_2 and 0·0940 H_2O. C = 66·32; H = 9·81.

$C_8H_{14}O_2$ requires C = 67·60; H = 9·86 per cent.

The product no longer reduced Fehling's solution; nor did it give Schiff's reaction; it still decolorised bromine water, and probably, therefore, contained an unsaturated alcohol.

Reduction of the Acid $C_8H_{12}O_3$ *by Hydrogen in Presence of Finely-divided Platinum:*—1·8 Grams of the acid (dried in a desiccator) were dissolved in about 10 c.c. of water, and reduced by shaking with finely-divided platinum in contact with hydrogen at 37° under a pressure of between 1½ and 2 atmospheres. When no more hydrogen was absorbed, the filtered solution of the barium salt was evaporated; a deliquescent salt remained, which was dried at 100°:

0·1454 gave 0·0745 $BaSO_4$. Ba = 30·12.

$(C_8H_{13}O_3)_2Ba$ requires Ba = 30·38 per cent.

$(C_8H_{15}O_3)_2Ba$ „ Ba = 30·11 „

The weight of hydrogen absorbed was calculated approximately as 0·0264 gram, whilst 1·8 gram of the barium salt would require 0·0322 gram of hydrogen to saturate it completely.

Reduction with Hydriodic Acid and Red Phosphorus:—Forty grams of the barium salt, $(C_8H_{11}O_3)_2Ba$, were heated for five hours with 320 grams of hydriodic acid solution (D 1·7) and 12 grams of red phosphorus. The mixture was diluted, and extracted with ether. After evaporating off the ether, the residual oil was left for twenty-four hours with zinc dust and dilute sulphuric acid, and then distilled in a current of steam. The distillate was neutralised with sodium hydroxide,* extracted with ether, and the ethereal solution evaporated to dryness; about 5—6 grams of a sodium salt were obtained, from which 4—5 grams of acid were isolated. On distillation, about 3—4 grams passed over below 200°,

* The ethereal extract contained a small quantity of a neutral oil with an aromatic odour; this was not further investigated.

and about 1 gram above 200°. The residue in the flask was converted into the barium salt:

0·1302 gave 0·0726 $BaSO_4$. Ba = 32·78.

$(C_8H_{15}O_2)_2Ba$ requires Ba = 32·39 per cent.

The fraction boiling below 200° consisted mainly of butyric acid. (Found, C = 53·57; H = 9·34. Calc., C = 54·54; H = 9·09 per cent.)

The fraction boiling above 200° was analysed:

0·1190 gave 0·2732 CO_2 and 0·1203 H_2O. C = 62·69; H = 10·11.
0·1450 „ 0·3340 CO_2 „ 0·1295 H_2O. C = 62·84; H = 9·93.

$C_4H_8O_2$ requires C = 54·54; H = 9·09 per cent.
$C_8H_{16}O_2$ „ C = 66·66; H = 11·11 „

This fraction was probably, therefore, a mixture of butyric and octoic acids, and was converted into the amides by Aschan's method (*Ber.*, 1898, **31**, 2348). The small amount of amide formed was recrystallised from petroleum and twice from water; about 0·1 gram (m. p. 103—104°) was thus obtained.

Raper's work on the condensation of aldol was repeated, and the same amide obtained in slightly larger amount; a mixture of the two amides melted at 103—104°. Each was separately mixed with a specimen of octoamide, prepared from Kahlbaum's pure octoic acid, and in neither case was there any lowering of the melting point; each amide was then added to ethylhexoamide (m. p. 101—102°), when the melting point fell to 96°.

The specimens of octoamide obtained from aldol and crotonaldehyde were now added together and analysed:

0·0754 gave 0·1845 CO_2 and 0·0810 H_2O. C = 66·74; H = 11·94.

$C_8H_{17}ON$ requires C = 67·13; H = 11·88 per cent.

LISTER INSTITUTE OF PREVENTIVE MEDICINE,
CHELSEA GARDENS, S.W.

CLXXXVI.—*Latent Heats of Vaporisation of Mixed Liquids. Part I.*

By DAN TYRER.

THE physical properties of mixed liquids have, for the most part, been fairly completely studied, and the general result that has been discovered is that for normal mixtures of unassociated liquids, the physical properties, as a general rule, are approximately linear functions of the composition, and in the cases of mixtures of associated liquids deviations from this additive law appear. One

physical property, however, seems to have been completely neglected, namely, the latent heat of vaporisation. It is not known whether or not the latent heat of a normal mixture is an additive quantity. When a mixture of two liquids is boiled, both its temperature and composition vary as the vaporisation proceeds, and hence its latent heat must also vary. It is clearly necessary to define the meaning of the latent heat of a mixture. Now a mixture of two liquids has, in two perfectly legitimate senses, two latent heats of vaporisation defined as follows:

(1) The latent heat of vaporisation of a mixture of two liquids is the heat required to evaporate one gram from an infinitely large quantity of the mixture of definite composition.

(2) The latent heat of a mixture of two liquids is the heat required to vaporise completely one gram of the mixture at constant temperature.

In the first definition no regard is paid to the composition of the vapour. Since an infinitely large quantity of the liquid is taken, both the temperature and composition of the parent liquid remain constant.

In the second definition the composition of the vapour is the same as the liquid, since all the liquid started with is assumed to have been vaporised. In order that the vaporisation may take place at constant temperature, the external pressure must be continually diminished as the vaporisation proceeds.

Since in the first case the external pressure is constant, we may term it the latent heat of vaporisation at constant pressure, and denote it by the symbol L_p.

In the second case the composition of vapour and liquid are the same, so we may term it the latent heat of vaporisation with constant composition, and denote it by L_c.

That the two quantities are quite separate and different in magnitude may be shown as follows:

Consider an infinitely large quantity of a mixture of two liquids A and B at its boiling point T. Let the composition in terms of the constituent A be C. Let one gram be evaporated, say, to avoid complications, under a negligibly small external pressure. The heat absorbed is L_p.

Now take one gram of the same mixture, and allow it to evaporate slowly in a vacuum at the same temperature T. Imagine the vaporisation to proceed in infinitely small successive quantities each of mass dm. The heat required to evaporate the first elementary portion will obviously be $L_p.dm$. Let us suppose, in the first place, that the constituent A is the one of higher boiling point, and also possesses the higher latent heat. Then as the evaporation of the

gram of liquid proceeds, the composition in terms of A will increase, and hence the heat required to vaporise successive elementary portions will continually increase until the heat required to evaporate the last portion will be $L_A\,dm.$, where L_A is the latent heat of vaporisation in a vacuum of pure A at the temperature T.

Obviously, the total heat required to vaporise the gram of liquid of composition C is equal to

$$L_c = -\sum_{L=L_A}^{L=L_P} L dm,$$

and must be much greater than L_p.

Expressing L as a function of the mass m of the unevaporated liquid, we can write:

$$L_c = \int_0^1 f(m)dm.$$

If, on the other hand, the constituent of higher boiling point, A, has the lower latent heat at the temperature T, the heat required to vaporise successive fractions will continually diminish, and L_p will be greater than L_c.

In this work latent heats at constant pressure (L_p) only have been measured.

Method of Determination and Apparatus.

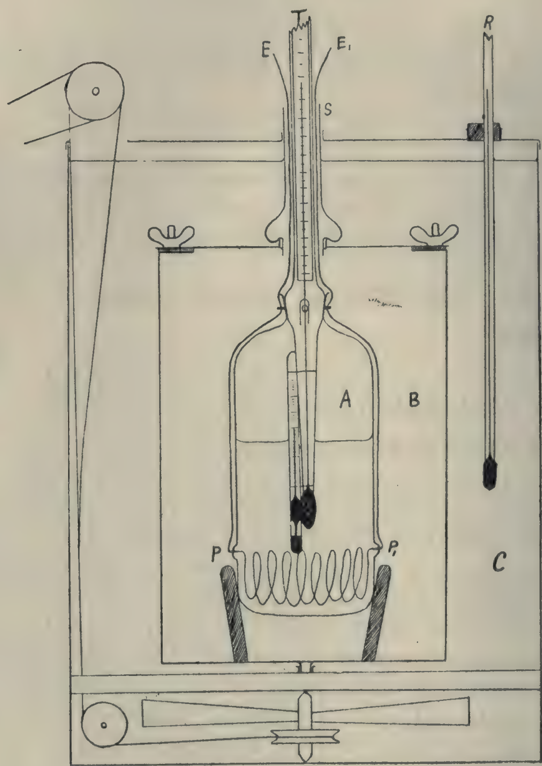
The latent heat of a pure liquid is a quantity which is by no means easy of measurement with accuracy, as a comparison of results obtained by different observers for the same liquid will show. With mixed liquids the difficulties are increased, for account has to be taken of changing composition and changing temperature as the vaporisation proceeds. There are two general methods of determining latent heats which have been fully worked out, namely, (1) condensation of vapour in a calorimeter, and observation of the heat evolved; (2) measurement of heat required to vaporise, by an electrically-heated wire, a weighed quantity of a liquid. An adaptation of the second method to mixed liquids is described in this paper.

The general principle of the method adopted is as follows: A known quantity of electricity is passed through a coil of platinum wire of known resistance, which is immersed in the liquid the latent heat of which is to be measured, first heated to its boiling point by an external bath. The amount of liquid evaporated is found by weighing before and after. This gives all the data necessary.

When, however, a mixed liquid is partly evaporated, the boiling point rises, and a certain amount of heat is used up in raising the

temperature of the liquid. To determine this correction a separate experiment is made to find the heat capacity of the liquid and the containing vessel, and the total rise in temperature is found by having a thermometer dipping into the liquid. In order that this rise in temperature may be small, a comparatively large quantity of the liquid is taken, and only a small quantity evaporated.

FIG. 1.



The general form of the apparatus is shown in the accompanying diagram.

The liquid the latent heat of which is to be measured is placed in the evaporating bottle A, which is about 250 c.c. capacity. This bottle is provided with a coil of platinum wire (about 1 metre of 0·02 cm. diameter), the ends of which are fused to two stout pieces of platinum, which are fused through the sides of the bottle at the points P, P_1. Stout pieces of copper wire are soldered to the platinum terminals, and pass outside to the ends E, E_1, which can

be attached to circuit leads. A thermometer T is ground into the neck of the bottle, and has a groove impressed in it, which can be turned opposite to a small hole pierced in the neck of the bottle, thus allowing it to be opened or closed to the external pressure. The bottle is made to stand on rubber-covered rods, as shown, in a copper insulating vessel B. This vessel is provided with a lid and two windows front and back (not shown in sketch). The lid and the panes of glass of the windows are screwed down on rubber to render the vessel perfectly water-tight. The vessel B is pivoted inside a large bath C, made of sheet copper, and provided with two windows (not shown). It contains water (or for temperatures higher than 100°, a high boiling liquid), and is heated by burners from below. It is provided at the bottom with a rotatory stirrer connected by a cord passing over pulleys to a small motor outside. The temperature of this bath is registered by a thermometer R. The vessel B can be rotated rapidly backwards and forwards by turning the glass tube S, and this serves to give the liquid in the evaporating bottle a rotatory motion, and continually sweeps fresh liquid over the platinum coils as the evaporation proceeds. Inside the bottle, attached to the thermometer, is a very small manometer, which serves to indicate when the pressure in the bottle has reached the atmospheric pressure.

The thermometers T and R are graduated in 1/5ths, and are readable to 0·02° with accuracy.

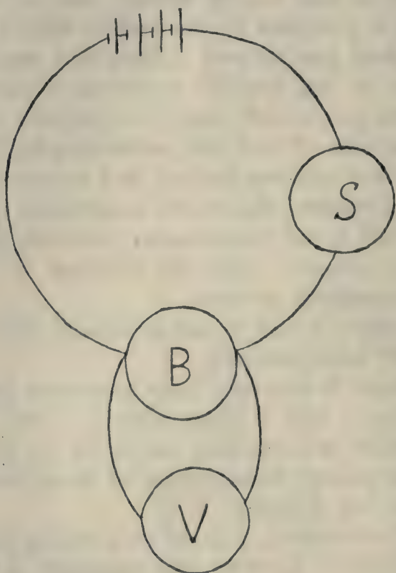
The current used is obtained from secondary cells (about eight cells are necessary), and is quite steady. The current passed through the circuit is accurately measured by means of a silver voltameter. The general arrangement of the apparatus is indicated in the accompanying diagram.

S is the silver voltameter, B is the evaporating bottle, and V is a Weston voltameter to measure the potential difference between the terminals of the platinum coil. This latter instrument covers a range of 8—13 volts, is graduated in 0·05 volt divisions, and is readable with accuracy to less than 0·01 volt. All the electrical contacts, where possible, were soldered to ensure perfect contact, and the switches were made tight, and were of a heavy type. The contacts were quite without resistance.

The composition of the mixed liquid is found before and after an experiment by determining the specific volumes of the liquid at a constant temperature, a table having been prepared beforehand, representing the relation between the composition and the specific volume. The specific volumes were determined with a quartz pyknometer immersed in a thermostat at about 20°, and the measurements were made to the fifth decimal place. The calculated

compositions contain an error not greater than 0·01 unit for mixtures the constituents of which differ moderately in their densities, whilst for mixtures like chloroform and benzene, which show a large variation of specific volume, an even greater degree of accuracy is obtained. About 5 to 12 grams of liquid are evaporated in each experiment. With mixtures like carbon tetrachloride and ether this causes a variation in composition of about 2 units, but with chloroform and benzene the variation is only about 0·2 unit. It is then assumed that over this small range the latent heat is a linear function of the composition, and the mean com-

FIG. 2.



position is taken as the point for which the latent heat is as determined in the experiment. The error of this assumption is negligibly small.

In carrying out an experiment, the boiling point of the mixed liquid is first determined approximately, and then its composition is found by determining with accuracy its specific volume. The evaporating bottle is about two-thirds filled, and weighed. The air is then pumped out of the bottle by pressing the end of the rubber tube which is attached to a strong water pump against the open orifice in the neck of the bottle, and when the liquid has boiled for a few seconds closing the bottle by turning the thermometer stem. The ground joint at the neck is lubricated with a

mixture of fused dextrose and glycerol. This lubricant is quite insoluble in organic solvents, and when made up to a proper consistency it answers the purpose admirably. It has the advantage over phosphoric acid as a lubricant, that it is more adhesive, and is not so easily squeezed out by pressure. It is also hygroscopic, but not to so great a degree as phosphoric acid.

After the air has been pumped out of the bottle it is again weighed to determine loss of liquid during the evacuation. A small correction is made to account for the very small change in the composition caused by this loss. The bottle is then placed in position in the inner copper vessel, and the external bath is heated to the boiling temperature of the mixture. The bottle and contents are slowly warmed by the passage through the platinum coil of a small shunted current. When the pressure inside the bottle has reached the external atmospheric pressure, as is indicated by the small manometer inside the bottle, and it has remained at a constant temperature for some minutes, the bottle is opened by turning the thermometer stem. The current is then switched on, and the boiling should commence immediately. The potential difference between the ends of the platinum coil should be from about 10 to 12·5 volts. As the temperature rises (usually about 1—1·5°) the temperature of the outside bath is raised correspondingly. A difference of a few tenths of a degree between the temperature of the boiling liquid and the outside bath makes no material difference during the time of an experiment, which only lasts about four or five minutes. As the boiling proceeds it is observed that the needle of the voltmeter always falls slightly, but this is only small (about 0·8 per cent.), and by taking readings at regular small intervals and finding the mean, the error in the voltage is reduced to about 0·07 per cent.

The total current passed through the coil is found by weighing the silver deposited on the platinum basin of the voltameter. About 0·3 to 0·45 gram of silver is usually deposited, and the error in weighing is not greater than 0·1 milligram. The temperature of the bath and bottle is allowed to fall about 3°, and the experiment is repeated with the bottle closed, and with a voltage of about 8·5. The rise in temperature is observed (about 4°), and the range covers that through which the temperature rose in the first experiment. This gives the heat capacity of the bottle and contents. The bottle is then weighed to determine the amount of liquid vaporised in the first experiment.

The latent heat is then calculated from the following equation:

$$L = \frac{J.S.V.}{A.M.},$$

where L is latent heat, J is electrical heat equivalent, S is weight of silver deposited during the experiment, V is the volts recorded on the voltmeter, A is the electrochemical equivalent of silver, and M is the weight of liquid vaporised. M is equal to the loss in weight of the bottle + the weight of vapour occupying the space vacated by the vaporised liquid at the boiling point. The latter, which is a small correction, can be approximately calculated.

A correction has now to be subtracted for the heat required to raise the temperature of the liquid during the vaporisation. This is:

$$H = \frac{C \times t \times W}{M},$$

where C is the heat capacity of liquid and bottle, t is the rise in temperature observed, and W is the mean weight of bottle and contents. C is found from the second experiment, and is given by:

$$C = \frac{J \times S_1 \times V_1}{A \times t_1 \times W_1},$$

where S_1 is weight of silver deposited, V_1 the voltage, t_1 the rise in temperature, and W_1 is the final weight of bottle and contents.

The corrected latent heat is then given by the following:

$$L_p = \frac{J}{A.M.}\left(SV - \frac{t}{t_1}.\frac{W}{W_1}.S_1V_1\right).$$

The correction need not exceed about 6 units, and is known with accuracy. The constant J/A has the value 213·60.

Three mixtures have been investigated, namely, ether and carbon tetrachloride; benzene and *n*-hexane; chloroform and benzene.

The results obtained are set forth in the remaining portion of the paper.

An idea of the general accuracy and practicability of the method is obtained by a comparison of results obtained for pure liquids with standard results obtained by other investigators.

The values given in the following tables for the latent heats refer to a mean pressure a few mm. above 760 mm. Without knowing variation of latent heat with variation of atmospheric pressure it is impossible to reduce all the values to one standard pressure. The difference, however, caused by a moderate change in external pressure makes but a very slight difference to the latent heat. The error is in any case well within total error of results.

Mixtures of Benzene and n-*Hexane.*

The benzene used in these experiments was prepared from Kahlbaum's pure material by refractionation over phosphoric oxide. It

was quite free from thiophen, and a litre distilled at constant temperature. Its specific volume at 20·00° was 1·13815.

Kahlbaum's pure hexane from petroleum was refractionated. Its specific volume at 20·00° was 1·47471.

Latent Heat of Benzene:—Three consecutive experiments gave the results:

	94·43	calories
	94·31	,,
	94·31	,,
Mean.........	94·35	,,

These values refer to a mean pressure of 763 mm., and a temperature of 80·35°. Griffiths and Marshall (*Phil. Mag.*, 1896, [v], **41**, 1) obtained the value 94·37. This result is probably the most accurate latent heat determination that has been made. J. C. Brown (Trans., 1905, **87**, 265) obtained the result 94·93.

Latent Heat of Hexane:—Two consecutive results gave:

	81·59	calories	
	82·11	,,	
Mean.........	81·85	,,	Temperature = 66·88°.

Mabery and Goldstein (*Amer. Chem. J.*, 1902, **28**, 66) obtained the result 79·4, which is rather considerably lower than the above.

Latent Heats of Mixtures of Benzene and Hexane:—The experimental results were plotted on cross-section paper against the composition, and the results given in the following table were read off from the smoothed curve. In the table also is given the boiling points of the mixtures for a mean pressure of about 766 mm.

Percentage of C_6H_6 in the mixture.	Latent heat in calories.	Boiling point.	Percentage of C_6H_6 in the mixture.	Latent heat in calories.	Boiling point.
0	81·85	66·88°	60	85·60	71·8°
10	81·93	67·55	70	87·20	73·2
20	82·15	68·6	80	89·03	75·1
30	82·55	69·1	90	91·27	77·4
40	83·24	69·9	100	94·35	80·45
50	84·26	70·8			

The above results for the latent heats of the mixtures contain estimated accidental errors of about 0·05 unit, but the series may contain a constant error of about 0·2 unit. The results are discussed at the end of the paper.

Mixtures of Carbon Tetrachloride and Ether.

Kahlbaum's carbon tetrachloride was refractionated; its specific volume at 20° was 0·62724. The ether used was prepared from absolute alcohol in the ordinary way. It was purified by washing

with acid, alkali, and water, and drying over calcium chloride and sodium. It was then fractionated, dried further over phosphoric oxide, and again fractionated; 500 c.c. distilled over constantly within 0·01°. Its specific volume at 20° was 1·40154 (Ramsay and Young's value=1·4015).

Latent Heat of Carbon Tetrachloride:—Three consecutive results gave:

	47·04	calories	
	46·86	,,	
	46·84	,,	
Mean.........	46·85	,,	Temperature=77·75°.

The first result was considered rather less accurate than the other two, and is excluded from the mean value.

Wirtz (*Wied. Ann.*, 1890, **40**, 446) obtained the result 46·35.

Latent Heat of Ether:—Three experiments gave the values:

	86·74	calories	
	86·06	,,	
	86·52	,,	
Mean.........	86·44	,,	Temperature=34·74°.

The following are results by other observers:

Wirtz (*Wied. Ann.*, 1890, **40**, 438) ...	88·39	calories.
Brown (Trans., 1903, **83**, 987)	84·78	,,
Ramsay and Young (*Phil. Trans.*, 1887, **178**, *A*, 90)	84·5	,,
Brix (*Pogg. Ann.*, 1842, **55**, 341)	90·0	,,
Andrews (*Quart. Journ. Chem. Soc.*, 1849, **1**, 27)	90·45	,,
Favre and Silbermann (*Compt. rend.*, 1846, **23**, 413)	91·11	,,

The results for ether appear to be very discordant. The latent heat of ether seems to be greatly affected by small amounts of impurities.

Latent Heats of Mixtures of Carbon Tetrachloride and Ether:—The following results were read from a smoothed curve of experimental values:

Percentage of carbon tetrachloride mixture.	Latent heat in calories.	Boiling point.	Percentage of carbon tetrachloride in mixture.	Latent heat in calories.	Boiling point.
0	86·44	34·75°	60	76·75	47·25°
10	86·30	36·15	70	73·00	50·80
20	85·50	37·60	80	68·47	55·77
30	84·05	39·40	90	61·60	64·65
40	82·15	41·65	100	46·85	77·75
50	79·85	44·25			

The above results are similar in point of accuracy to those in the previous case.

Mixtures of Chloroform and Benzene.

The chloroform was prepared from commercially "pure" material as follows. It was washed with acid, alkali, and water, and then distilled under a layer of dilute alkaline solution of potassium permanganate. The product was dried over calcium chloride, fractionated, dried further over phosphoric oxide, and again fractionated. About 2 litres distilled over within 0·03°. Its specific volume at 20° was 0·67219, and it boiled at 61·40°/758 mm.

Latent Heat of Chloroform:—Three experiments gave the results:

	59·38	calories
	59·27	,,
	59·24	,,
Mean.........	59·29	,, Temperature = 61·52°.

Wirtz (*Wied. Ann.*, 1890, **40**, 446) obtained the value 58·49.

Data concerning the benzene have already been given.

Latent Heat of Mixtures of Chloroform and Benzene:—The results given in the following table were obtained from a smoothed curve of experimental results.

Percentage of chloroform in the mixture.	Latent heat in calories.	Boiling point.	Percentage of chloroform in the mixture.	Latent heat in calories.	Boiling point.
0	94·35	80·65°	60	70·13	71·75°
10	90·00	79·58	70	67·15	69·50
20	85·55	78·40	80	64·50	67·00
30	81·25	77·12	90	61·83	64·30
40	77·15	75·58	100	59·29	61·52
50	73·40	73·80			

Discussion of Results.

The relation between the latent heat at constant pressure and the composition is best shown graphically.

It will be seen from the figure that the latent heat is by no means a linear function of the composition, as might have been expected. There is a relation which holds fairly closely in two cases between the latent heat and the boiling point. This can be shown by testing the well known relation of Trouton:

$$\frac{LM}{T} = K,$$

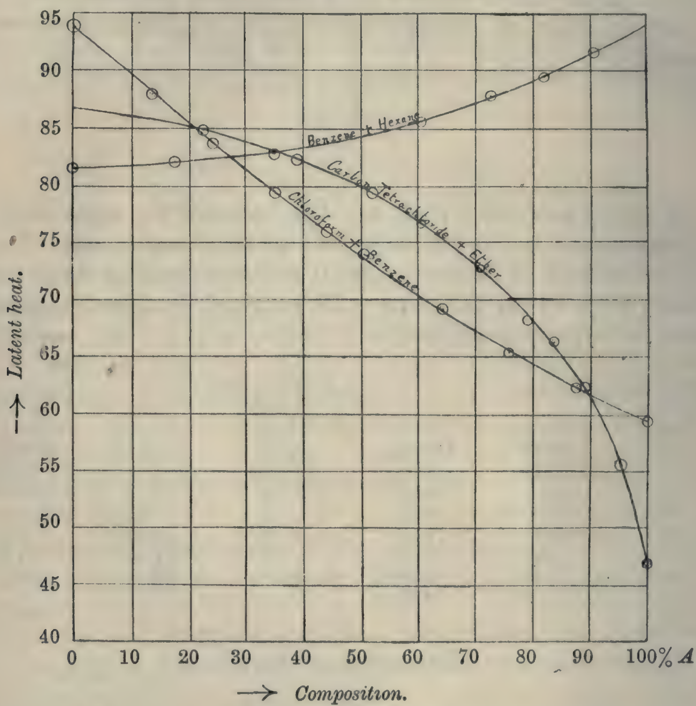
where L is the latent heat, M the molecular weight, and T is the temperature of boiling on the absolute scale.

In the case of mixtures, M must be taken as the mean molecular weight given by the formula:

$$M = \frac{100}{\frac{C}{M_A} + \frac{100 - C}{M_B}},$$

where C is the composition in terms of the constituent A, and M_A and M_B are the molecular weights of the pure constituents. In

FIG. 3.



the following table are given the values of the constant $K = LM/T$ for the three cases.

While the value for K in the first and third cases is fairly constant, there is an entire lack of constancy for the case of carbon tetrachloride and ether.

Now Trouton's equation is directly deducible from the relation:

$$LM = K_1 T \log \frac{V_v}{V},$$

Composition C.	Values of K for mixtures of benzene and hexane.	Values of K for mixtures of carbon tetrachloride and ether.	Values of K for mixtures of chloroform and benzene.
0	20·74	20·85	20·83
10	20·51	21·86	20·66
20	20·31	22·75	20·42
30	20·15	23·60	20·24
40	20·07	24·40	20·05
50	20·07	25·08	20·01
60	20·13	25·77	20·04
70	20·23	26·23	20·24
80	20·35	26·36	20·48
90	20·52	25·34	20·84
100	20·83	20·55	21·06

where T is the temperature, V_v and V_L are the specific volumes of vapour and liquid respectively at T, and K_1 is a constant. This relation, moreover (see Crompton, Proc., 1901, **17**, 61; and Kleeman, *Phil. Mag.*, 1910, [vi], **20**, 665), depends on the assumption that the composition of the vapour is the same as that of the liquid. We should expect, therefore, that Trouton's equation will only hold for mixtures when the difference between the composition of the liquid and the saturated vapour is comparatively small. Of the above cases this difference is greatest in the case of carbon tetrachloride and ether, and this case, as has been seen, shows the greatest divergence.

It is fairly clear that the latent heat of a liquid at constant pressure, although it is a function of the composition of the mixed liquid, is, at the same time, largely a property of the vapour, and dependent on the composition of the vapour.

It is hoped in subsequent papers to extend the present investigations to other classes of mixtures, and to study the relation between the latent heat and the composition of the vapour which is in equilibrium with the liquid of known composition.

The author is indebted to Mr. J. I. Crabtree, B.Sc., for much valuable assistance in the early stages of the work.

THE CHEMICAL LABORATORIES,
THE UNIVERSITY, MANCHESTER.

OBITUARY NOTICES.

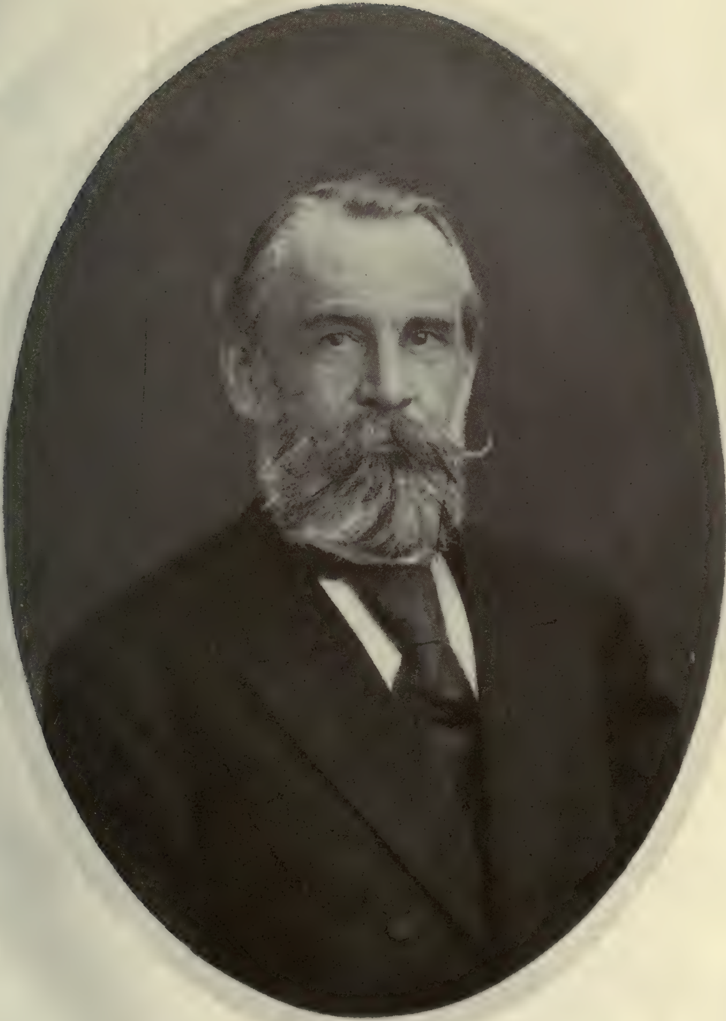
FRIEDRICH KONRAD BEILSTEIN.

BORN FEBRUARY 17TH, 1838; DIED OCTOBER 18TH, 1906.

THE honorary membership of the great learned societies is a testimony of admiration for the brilliant work done by its recipients. In the case of Beilstein it was more; it was, above all, an expression of deep personal gratitude of innumerable chemists, whose own scientific work had been in no small way advanced and helped by that most marvellous product of an unusually clear and systematic mind, Beilstein's "Handbuch der Organischen Chemie." To the production of this book Beilstein not only devoted his whole life, but he also sacrificed, especially in later years, many opportunities for original experimental work, which, if he had been able to utilise them, would have materially added to his claims for our admiration as a master of experimental research.

Born on February 5/17th, 1838, in St. Petersburg, Beilstein was, like so many of the inhabitants of the great northern capital, German by descent, but a Russian in his nationality and his complete mastery of the difficult language of his adopted country. After receiving his first education in one of the excellent German schools of his native city, he left, a very precocious youth of only fifteen years of age, for Heidelberg, where he studied chemistry under the excellent tuition of Bunsen. After two years he moved to Munich, and became a pupil of Liebig. Very soon, however, he returned to Heidelberg, where he had occasion to join that remarkable group of distinguished young scientists then living in that beautiful city—Roscoe, Lothar Meyer, Landolt, Pebal, Lieben, Quincke, Baeyer, and others. In animated discussions with these and other friends Beilstein gradually acquired the interest and preference for organic chemistry, which henceforward became the special domain of his own scientific research.

It was this increasing love for the problems of organic chemistry which led him once more to change his place of residence and to move to Göttingen, where Wöhler, then still in the prime of his life and scientific activity, attracted a large circle of enthusiastic admirers and collaborators. Following in the great master's footsteps, Beilstein began his own research work with investigations in the cyanogen group, one of which, an elegant study of murexide,



F. Beilstein

he used as a dissertation for taking his degree as a Ph.D. in February, 1858, two days before completing his twentieth year.

Beilstein was ever anxious to increase his skill and experience. With the intention of so doing, he went to Paris, and there became an assiduous pupil of Adolphe Wurtz in his laboratory in the École de Médecine. Here he associated with Friedel, and his work during this period, referring to the action of sodium ethoxide on ethyl and other acetates, bears testimony of this friendship. At the same time he went deeper and deeper into the study of chemical theories, until he decided to devote his whole life to pure science and to an academical career.

With this intention Beilstein accepted a situation as laboratory assistant at Breslau offered to him by Loewig in the autumn of 1859, but he soon exchanged it for a better one at Göttingen. Here he remained for six years, until 1866, when he was called back to St. Petersburg to fill a professorship in his native city.

Beilstein's official position in Göttingen was that of a laboratory assistant, but he soon obtained the "venia legendi," and lectured as a "Privatdocent" on organic chemistry. In 1865 the faculty conferred on him the dignity of a "Professor extraordinarius." Beilstein's life in Göttingen was one of incessant activity as a teacher and an investigator. He was connected by intimate friendship with his colleagues Fittig and Hübner, and jointly with them he accepted the task of editing the *Zeitschrift für Chemie*, founded by Kekulé, and important to this day as a source of information.

Here in Göttingen Beilstein found that field of experimental research which was destined to prove most fruitful in his hands, the study of the isomerism of the derivatives of the benzene series. He began this work with the brilliant discovery of the relations existing between chlorotoluene and benzyl chloride. He then embarked on an elaborate investigation of the isomerism existing between the various chlorinated benzoic acids and other members of the aromatic group. Occasionally he also turned his attention to problems of the aliphatic series.

It was in Göttingen that Beilstein began to collect the systematic notes on organic compounds which finally led to the production of his famous handbook. No doubt they were originally only meant for his own information and reference, but he took an ever-increasing pride and pleasure in keeping them complete in spite of the rapid growth of the chemical literature, and in later years he became aware of their extraordinary value and utility as a work of reference for all chemists engaged in the investigation of organic compounds. He found an able publisher in the firm of Leopold

Voss, in Hamburg. The first edition, which Beilstein compiled practically without help, appeared in 1881 in two volumes, and was rapidly exhausted. The second edition began to appear in 1886, and filled three volumes of larger size than the first; the third edition was commenced in 1893, and its four volumes may almost be called unwieldy. It was finished in 1900, and has been supplemented, as everyone knows, by four large volumes of additions edited by the German Chemical Society, which became the proprietor of the handbook and the heir to Beilstein's immortal creation. The fourth edition, now in progress, is expected to assume the size of a small library.

Beilstein's handbook is, in its completeness, its short and concise, yet exhaustive, wording, the most perfect work of reference ever compiled for any domain of human knowledge. At the same time it forms a faithful mirror representing the extraordinary growth of research in the field of organic chemistry. Already the handbook itself has grown, in spite of the marvellous clearness of its system, too large to be used in the ordinary way of referring to such books. But supplemented, as it now is and for ever will be, by Richter's equally marvellous index, it will hold its own in future days as a brilliant proof that even the most complicated subjects may be clearly registered by a systematic genius such as it was the good fortune of chemical science to possess in Beilstein.

In 1866 Beilstein returned to his native country, where he became Professor of Chemistry at the Imperial Technological Institute of St. Petersburg. As an investigator he continued in his new position the work to which he had devoted himself in Göttingen. Jointly with a few collaborators, such as Kuhlberg, Kurbatoff, and others, he published a large number of researches of lasting value, referring almost exclusively to the phenomena of isomerism of the aromatic series.

In 1881 Beilstein became a member of the Russian Academy of Sciences, a position with which is associated a good income, a private dwelling, and a laboratory. He was soon able to retire from his professorship, and to live entirely for research, the compilation of his handbook, and his favourite pastime, music. He was also very fond of travelling, and invariably spent several months of the year in Germany and other countries of Europe. After visiting his old friends and making new acquaintances in the chemical world, he generally settled himself in some beautiful spot in the Tyrol or in Switzerland, studying the lovely scenery of the mountains, but never omitting to devote several hours a day to the handbook which had become an integral part of his life. He almost seemed to have lost something, when, in 1900, this work came, for him, to an end,

and passed entirely into the hands of the German Chemical Society.

Beilstein remained a bachelor all his life, but he had an adopted daughter, who was his companion in later years, when, by losing some of his best friends, he began to feel solitary. In 1904 this young lady married an officer of a regiment stationed at Kiew. In 1905 Beilstein took a long journey to France, followed by a stay at Baden-Baden. For 1906 he planned a stay at the Riviera, but Fate would have it otherwise. On October 5/18th, 1906, he died quite suddenly in an apoplectic attack.

Beilstein was a genial and most amusing companion, full of humour, and inclined to be caustic and sarcastic, although good-natured, in his quaint and witty remarks on mankind and its doings. He had a brilliant memory, and an inexhaustible fund of information on every possible subject. His life was a beautiful example of devotion to science; it was well spent, and well filled by the fixity of its purpose.

OTTO N. WITT.

EMIL ERLENMEYER.

BORN JUNE 28TH, 1825; DIED JANUARY 22ND, 1909.

RICHARD AUGUST CARL EMIL ERLENMEYER, whose death occurred on January 22nd, 1909, was the son of Dr. Friedrich Erlenmeyer, a Protestant divine, and was born in Wehen, near Wiesbaden, on June 28th, 1825. After passing his Maturitäts Examination in 1845, his intention was to study medicine, and, with this object in view, he proceeded to the University of Giessen, where he attended Liebig's lectures, which, together with the personality of Liebig, had such an effect on the young student that he soon decided to devote himself entirely to chemistry. In the summer of 1846 he went to Heidelberg for one year, and studied physics, botany, and mineralogy under Jolly, Bischof, and Leonhardt, returning to Giessen in 1847.

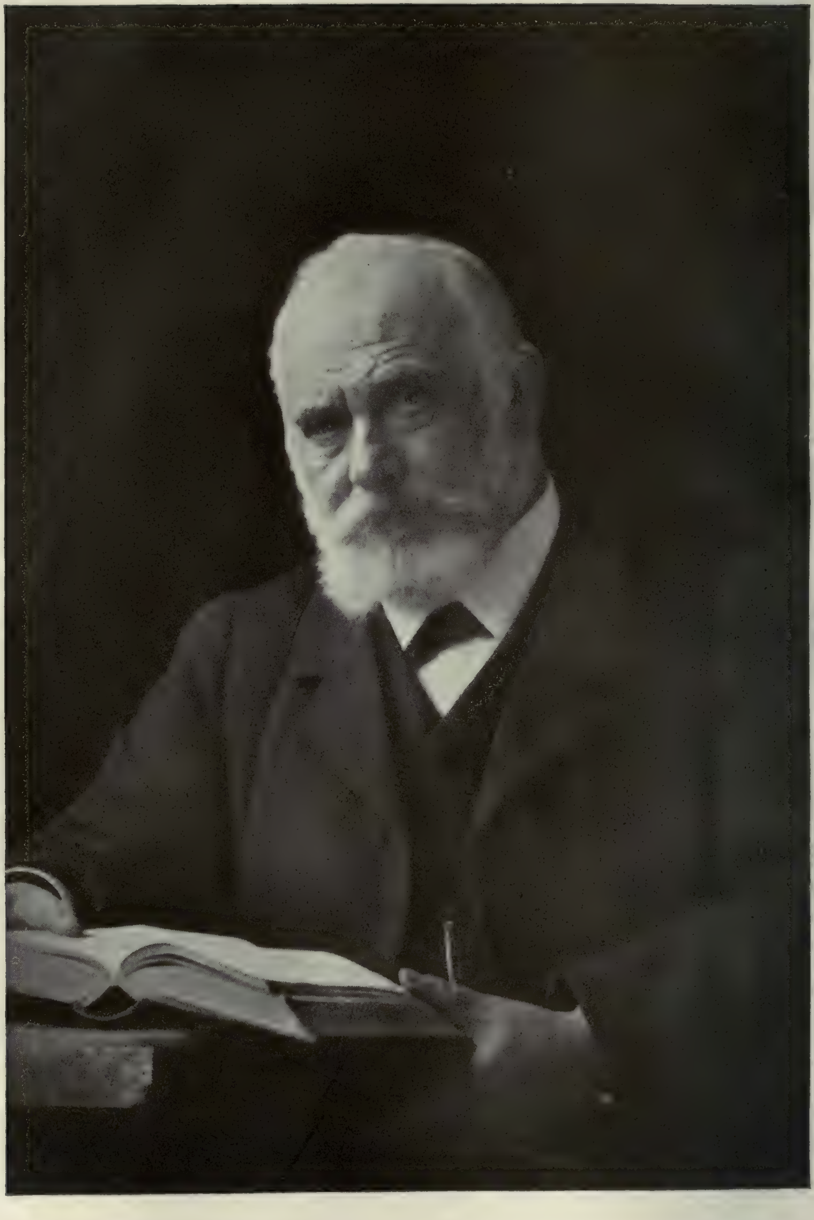
After serving as assistant to H. Will, and subsequently in the same capacity to Fresenius, Erlenmeyer decided to devote himself to pharmaceutical chemistry, and to this end he studied in Nassau, where he passed the State pharmaceutical examination, and shortly afterwards acquired an apothecary's business, first at Katzenellenbogen, and subsequently in Wiesbaden. Pharmacy appears to have had no charm for Erlenmeyer, and, in order to follow the career of a teacher, he graduated in Giessen in 1850, and in 1855 proceeded to Heidelberg in order to devote himself entirely to chemistry. There he converted a shed into a private laboratory,

in which he carried out investigations for works, and, in the capacity of expert, he had frequent occasion to visit France and England. In 1857 Erlenmeyer became "Privatdocent," and his thesis, "On the manufacture of the artificial manure known as superphosphate," contained a description of several crystalline substances which greatly interested Bunsen. It was while at Heidelberg that Erlenmeyer was brought under the influence of Kekulé, whose theoretical views he was one of the first to adopt, and subsequently, on the removal of Kekulé to Ghent in 1859, his laboratory became the centre of organic chemistry in Heidelberg. The success of his teaching led the University of Heidelberg to make him extraordinary Professor in 1863, and in 1868 he was called to Munich to take charge of the fine laboratories of the new Polytechnic School, a post which he held until his retirement from teaching in 1883. During these years he worked with ceaseless energy as an investigator, and especially as a teacher, and the success of his teaching was doubtless due in great measure to the amount of time and energy which he devoted to the personal instruction, not only of the advanced students, but also of beginners. Many of Erlenmeyer's most valuable publications deal with problems of theoretical chemistry, and in most of these the influence of Kekulé is very marked; two of his most important achievements are doubtless the suggestion of the formula for naphthalene, which is still in use, and his statement of the well-known law, to which his name became attached. According to this law, unsaturated alcohols, $>C{:}CH{\cdot}OH$ and $>C{:}C(OH){\cdot}C{<}$, are incapable of existence, and are converted, at the instant of formation, into aldehydes and ketones by intramolecular change, a law which does not now hold good in all cases, but which, at that time, was a true statement of the facts as they were then known.

Erlenmeyer's practical investigations were concerned mostly with problems in the aliphatic series. In 1859 he succeeded in synthesising aminohexoic acid, an important investigation, which led him to study the general behaviour of albuminoids on hydrolysis. He worked out methods which enabled him to determine the relative amounts of leucine and tyrosine which are produced during the degradation of several substances of this class, and these researches, carried out with great care and skill, may be said to have served as models for other investigators in the same field.

He was the first (1860) to understand clearly the nature of glycide, and to suggest that this substance is related to glycerol in the same way as is metaphosphoric acid to orthophosphoric acid; in the following year he studied the action of hydriodic acid on glycerol, and showed that the product is *iso*propyl-, and not propyl-,

1650a



Fittig

iodide, as Simpson had asserted. In conjunction with Wanklyn, he subsequently employed the same process in the cases of mannitol and dulcitol, and obtained *sec*-hexyl iodide. The investigations of Erlenmeyer on the higher alcohols produced during alcoholic fermentation yielded the important proof that these alcohols do not belong to the normal series. He showed that fermentation "butyl alcohol" is converted by oxidation into *iso*butyraldehyde and *iso*butyric acid, and was able to synthesise the latter from *iso*propyl iodide by conversion into the cyanide and subsequent hydrolysis.

Other researches which may be mentioned are the isolation of glycollic acid from unripe grapes (with Hoster, 1864); the synthesis of sodium oxalate by the action of heat on sodium formate (1868); the study of the conditions under which ether is hydrolysed to alcohol (with Tscheppe, 1858); the synthesis of phenyl-lactic acid (1880); the preparation of pyruvic acid by the distillation of tartaric acid (1881); and the formation of carbostyril from quinoline (1885).

The investigations in the aromatic series include an important series of papers on the isomerism of the cinnamic acids, and also an interesting paper published in 1882, in conjunction with Lipp, on the synthesis of tyrosine from phenylalanine.

In 1875 Erlenmeyer carried out (with Widnmann) an important investigation on the nitration of benzoic acid, in which he definitely disproved Fittica's statement that more than three nitrobenzoic acids exist. He was also able to disprove, in a series of very careful investigations carried out in conjunction with Kayser, F. Fischer, and Lipp, the statement of Wislicenus (1863) that the lactic acid produced from the product of the action of potassium cyanide on ethylene chlorohydrin, and also contained in small quantities in meat extract, is different from the hydracrylic acid obtained by Beilstein from β-iodopropionic acid.

W. H. P.

RUDOLPH FITTIG.

Born December 6th, 1835; Died November 19th, 1910.

Rudolph Fittig, who died somewhat unexpectedly in November 1910, was born in Hamburg in 1835. He was a student under Limpricht at Göttingen, becoming "Privatdocent" in the University in 1860 and honorary professor in 1866. In 1870 he was appointed professor in the University of Tübingen, and transferred in 1876 to the University of Strasburg as successor to A. Baeyer. As professor and director of the Chemical Institute

of this last University, he carried on with conspicuous success to the end of his life the teaching and research for which this Institute has become so generally renowned in the scientific world. It is of interest to add that during his early life at Göttingen he served for a short time as assistant to Wöhler.

Fittig's originality as in investigator became manifest at the beginning of his career. The well-known synthetical process for preparing the homologous hydrocarbons of the benzene series by the action of sodium on a mixture of the haloid derivatives containing the required radicles was his first important contribution to organic chemistry. The researches which laid the foundation of this still valuable method commenced as far back as 1862 with the discovery that diphenyl was formed by the action of sodium on monobromobenzene. The further developments of this work in the direction of determining the constitution of the isomeric hydrocarbons by means of the products obtained by the successive oxidation of the side-chains have become so intimately incorporated into our modern text-books that their authorship is apt to be overlooked by the modern student. Among his early discoveries must also be included the hydrocarbon phenanthrene, which was isolated from coal tar and characterised about the same time (1872) by Graebe and by Fittig and Ostermayer.

Another line of work with which Fittig's name will be always associated is that exhaustive series of researches upon unsaturated acids and lactones which he commenced in 1873 with Ira Remsen, and which were continued with various colleagues for over twenty years. A summary of this work was given before the German Chemical Society in 1894. Here again he enriched chemical science by a succession of discoveries which have now become common knowledge, and the lecturer who discourses before his class about the complicated isomeric relationships between itaconic, citraconic, and mesaconic acids and their derivatives is really giving an account of Fittig's results. Of this work certain developments stand out conspicuously, notably the synthesis of coumarone from coumarin (Fittig and Ebert, *Annalen*, 1882, **216**, 168), the preparation of the complete set of six optically active and inactive modifications of phenylparaconic acid commenced in 1882 (Fittig and Jayne, *ibid.*, 108), and, above all, the synthesis of α-naphthol from phenyl*iso*crotonic acid, which at the time of its announcement was at once recognised as a discovery of the first order of importance in connexion with the question of the constitution of naphthalene derivatives (Fittig and Erdmann, *Ber.*, 1883, **16**, 43; *Annalen*, 1885, **227**, 242).

It would be impossible to do full justice to the immense array

Hans Landolt

of discoveries for which we are indebted to Fittig within the compass of this notice. His work is characterised generally by the substantial body of experimental evidence on which his conclusions are based. In theoretical matters he did not display much speculativeness, and yet one of his suggestions has turned out to be one of the most prolific sources of formula reconstruction among cyclic compounds ever introduced into organic chemistry. It was Fittig who, in 1873, first showed that the formula of benzoquinone might be written on the double ketonic type by making the phenylene residue of the benzene ring quadrivalent instead of bivalent, as in the earlier "peroxide" formula of Graebe. The so-called "quinonoid" structure, which is now so liberally assigned to all sorts of aromatic compounds, is in fact Fittig's "ketonoid" conception applied to particular cases.

In addition to his original papers Fittig contributed to general chemical literature the "Grundriss der organischen Chemie" (1872; 11th ed., 1886–87), and he edited the revised edition of Wöhler's "Grundriss der organischen Chemie" (10th ed., 1877). He collaborated with Beilstein and Hübner in editing the new series (1865–1871) of the *Zeitschrift für Chemie*, and from 1895 he was one of the editorial staff of Liebig's *Annalen*.

R. M.

HANS HEINRICH LANDOLT.*

BORN DECEMBER 5TH, 1831; DIED MARCH 15TH, 1910.

ON the 15th of March, 1910, died one of the oldest members of the present generation of chemists, the patriarch of physical chemistry, Hans Heinrich Landolt. He was born on the 5th of December, 1831, in Zurich, and had thus reached the ripe age of seventy-eight years, having enjoyed the good fortune of not having outlived himself. He will remain in the memory of his scientific colleagues and in the hearts of his friends and relatives as active and full of life to the end.

"Landolt was a scion of the old and respected patrician family of Zurich, to which belonged Salomon Landolt, whom Gottfried Keller has portrayed so admirably in his 'Züricher Novellen' as 'Der Landvogt von Greifensee.' This ancestry was unmistakably evident in his entire personality: simple and upright, homely, and yet full of native dignity, free in thought, feeling, and action, entirely without any religious or political superstition, Landolt was the prototype of the free and sturdy Swiss citizen." These

* Adapted from the obituary address by the late Professor J. H. van't Hoff (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910).

admirable words of his lifelong fellow-worker, Professor Brühl, may serve to introduce the portrait of our universally respected and beloved foreign Fellow.

Landolt's early life in Zurich was happy and free from care. He was industrious, even as a child, and soon displayed his scientific proclivities by devoting himself passionately, at the cost of his grandparents' carpets and curtains, to chemical experiments and fireworks; flame and light were destined on many later occasions to play a prominent part in his more serious researches.

At the age of nineteen Landolt entered the University of his native town for the study of chemistry and physics, attending the lectures of Löwig; and in the same year his first work, on "Stibmethyl," appeared in the "Schriften der Naturforschenden Gesellschaft" in Zurich. Shortly afterwards appointed assistant to Löwig, he followed him in 1853 to Breslau, for owing to his parents' decease, his ties to his native land were loosened; nevertheless, he kept in touch with the town of his birth, and maintained personal relations with his numerous friends by annual visits.

Before Landolt settled, he filled appointments in Berlin and Heidelberg, and again for a short period in Breslau.

At first, in 1853, while still in Breslau under his chief Löwig, he obtained the degree of Doctor of Philosophy on the strength of a dissertation, "Ueber die Arsenäthyle." This research, arising directly from his first work, proved of great importance to the law of valency. Then followed his journey to Berlin, the chief cause of which was the presence of Mitscherlich, Rose, Johannes Müller, and Dubois, whose lectures he attended. Facilities for experimental research in a chemical laboratory were, however, at that time practically non-existent in Berlin; he therefore left for Heidelberg, where Bunsen, whose personality had attracted Landolt whilst he was still in Breslau, had just commenced work in a newly-founded institute.

His experience in Heidelberg, and especially Bunsen's influence, had a great effect on the direction of Landolt's development, and he loved to dwell on the recollection of those times and on Bunsen's character, which was in many respects akin to his own.

He lived together with von Pebal in the Meierei near the old chemical laboratory in the Hauptstrasse. To the common dinner table at the Bayrische Hof came, among others, Lothar Meyer, August Kekulé, Beilstein, Bahr (subsequently assistant-professor in Upsala), Frapolli (afterwards in Milan), Pavesi (later in Pavia), Goupillat (afterwards in Sèvres), and also Adolf Wagner, of Berlin.

Landolt and Quincke used to work together in the new institute in the small gas-room with two benches.

After devoting himself for a short time to the electrolytic production of calcium and lithium, Landolt started an investigation of the gases produced in the Bunsen burner, which had been constructed in the winter 1854–55. Association with Quincke in work, as well as in frequent week-end excursions into the surrounding country, resulted in a friendship which was severed only by death.

In 1856 Landolt returned to Breslau, where he was soon afterwards joined by Lothar Meyer and Beilstein, and in the same year he became a lecturer in chemistry on the strength of his monograph on "Chemische Vorgänge in der Flamme der Leuchtgase."

In the year 1857, at the early age of twenty-six, he was called from Breslau to Bonn, being the youngest "Extraordinarius" in Prussia. Chemistry was there represented at that time by Bischof, the chief professor of chemistry and technology, and by Baumert; pharmacology by Bergemann. With all of these Landolt soon entered into cordial relations. Other members of his circle of friends at Bonn were Usener, Schönfeld, Pflüger, and subsequently Bettendorf, who was Landolt's assistant for some time, as well as Horstmann, his pupil, collaborator, and life-long friend. In his new position Landolt commenced his great and fundamental researches on the influence of the atomic composition of liquids containing carbon, hydrogen, and oxygen on the transmission of light; they were published during the years 1862 to 1864 in Poggendorf's *Annalen*, and were largely stimulated by Pflüger, one of Landolt's many friends in Bonn, as well as by the mathematician and physicist Beer. These investigations were a continuation of the previous researches of Gladstone and Dale, but championed in particular the new points of view opened out by the laws of constitution, then in process of formulation, which finally rendered possible the calculation of the refractive power of the chemical molecule from the refractivities of its constituent atoms, by taking into consideration the manner in which these are linked together. Landolt in later years undertook the solution of many of the problems raised by these magnificent researches of his youth. For after the notable investigations of Hertz (1887—1888) had demonstrated the identity of optical and electric propagation, and had shown that light waves are differentiated from electric waves merely by vast difference in size, Landolt (1892), in collaboration with Jahn, again took up his former line of work, determining the molecular refractivity of organic substances for rays of very great wave-length, that is, electric waves. In general, relations were

found similar to those of light-rays, with, however, several remarkable differences which remain as yet incompletely explained.

At Bonn, in 1859, Landolt began at an early age his happy family life by marrying Milla Schallenberg, the amiable and beautiful daughter of Swiss parents settled in Bonn.

On Bischof's resignation August Wilhelm Hofmann was called from London to Bonn, where, as the result of his urgent representations, the most extensive chemical institute in the world at that time was erected. But before the building was completed, Hofmann had accepted a chair in Berlin, his place at Bonn being taken by August Kekulé, who came from Ghent. To him and to Landolt, who was appointed to a full professorship, and who had meanwhile completed his classic research on the vapour-pressure of homologous compounds, was assigned in 1867 the direction of the new institute, and these two men, occupied in totally different spheres of scientific activity, worked in complete harmony in the administration of their laboratory. As early as the year 1869 Landolt was appointed to the head of the newly-founded technical college at Aix-la-Chapelle, where a stately chemical institute was built according to his plans.

The time spent in Bonn remained in Landolt's memory as the most pleasant period of his life, and in his last years he entertained serious thoughts of retiring to that town. This plan, however, was not carried out, although he selected Bonn as his last resting-place.

Landolt's first task in Aix-la-Chapelle was the erection of the new institute, in which work he had the help of his assistant, the late Professor Brühl. The very best was aimed at, with perhaps exaggerated detail, for it is impossible to deny that, to a casual visitor, the building appears unnecessarily complicated. On the other hand, many novel and useful arrangements were installed, for example, an electrically illuminated projecting-lantern was introduced by Landolt in his theatre, and at once became an indispensable aid to demonstration.

Landolt's investigations were carried out from the point of view characteristic of the physical chemistry of that period: the relations between physical properties and chemical constitution. In accordance, however, with the more practical side of a technical college, polarised light, which is of great importance in the sugar and other industries, was now accorded especial attention. Ample success crowned his efforts. His admirable researches ("Ueber das Vermögen organischer Körper, das polarisierte Licht zu drehen") exhausted the entire field; Landolt made his name famous throughout the world of science and technology by his classical experimental

work on this subject, by improvements and novel designs in polarimeters, as well as by his standard book on "Das optische Drehungsvermögen organischer Substanzen" (1879); the second edition of this work, prepared by him in 1898, is even to-day unquestionably a classic, and a most exhaustive and trustworthy compendium of polarimetry. Of his scientific achievements in this field, the most prominent is the law, which will undoubtedly remain for ever associated with his name, that the rotation of salts of active acids and bases in aqueous solution may be calculated from constants corresponding with each acid or base, and is independent of the nature of the salt. Stereochemistry, moreover, is indebted to Landolt for vigorous aid at its rather difficult birth, through the support of its laws by his undisputed authority in the domain of optical activity.

These purely scientific achievements gained the respectful attention of representatives of the law, of technical industries, and even of agriculture, owing to the fact that the polarimeter, in conjunction with Landolt's measurements of optical rotatory power, plays so considerable a part in analysis and standardisation in the manufacture of sugar, alkaloids, terpenes, camphor, and scents. Wherever an industry begins to develop, a collector of excise is certain to be close at hand. It has thus come about that the name of Landolt is known to customs officers, and even to agriculturists, with whom he certainly had otherwise but little in common. For the same reason, also, Landolt was called in 1880 by the Prussian Ministry of Agriculture to the newly-founded Agricultural College in Berlin, where he remained until the year 1891.

At the Agricultural College he was again called upon to construct and reconstruct his laboratories, collaborating during these years with Dr. Börnstein in the compilation of the well-known "Physikalisch-chemischen Tabellen," the preparation of which was distinguished by the greatest care and accuracy. The third edition, brought out in 1905 with the assistance of Professor Meyerhoffer, and generously subsidised by the Berlin Academy of Sciences, is of so indispensable a nature that a project has been advanced by the International Congress of Applied Chemistry for an international committee to publish periodical editions of tables of this character.

In the year 1882 Landolt became a member of the Berlin Academy. To this period are to be ascribed the highly remarkable investigations into the velocity of the reaction between iodic acid and sulphurous acid (*Sitzungsber. K. Akad. Wiss. Berlin*, 1885—1886). This reaction, the mathematical calculation of which, attractive as the problem is, has remained unsolved to the present

day, is one of those in which the time-period is most accurately determinable in advance from experimental data.

In 1891 Landolt was appointed, as successor to Karl Rammelsberg, director of the second chemical institute of the Berlin University. This position he occupied until his retirement from active life in 1905, an occasion on which he was awarded the Great Gold Medal for Science and Art. His experimental work at this period bears, in a marked degree, the stamp of infinite patience, and is directed less towards the acquisition of new points of view and of new methods than that previously referred to.

The series of investigations was opened by a number of most careful determinations of melting points, large quantities of the substances under examination being prepared in the highest possible degree of purity. The results obtained were connected with the determination of molecular weight, the importance of melting points in this respect having gradually become recognised. Then followed a series of investigations relating to the problem whether crystalline substances could by extreme comminution be deprived of their crystalline structure. An ingenious suggestion—that the optical activity of sodium chlorate in the crystalline form could be traced from step to step—permitted this question to be definitely decided in the negative. It is evident that the state of division obtained in those preparations did not remotely approach the possibility of separating molecule from molecule.

The third, last, and perhaps most remarkable series of investigations related to the question of the possibility of change in weight during chemical reactions. This problem, which had been dealt with by Lavoisier in the first half, and by Stas in the second half of the nineteenth century, was now, with the aid of the most perfect apparatus, again taken up, and was continued for over ten years. The re-examination of the facts, which, as is well known, led to a negative result, was carried out most opportunely, immediately preceding as it did the discovery of the altogether unexpected phenomena of radium which appeared to assail the fundamental laws of experimental science.

We may form some idea of the devotion required by these accurate experiments of Landolt when we consider the expenditure of time which they involved. But in addition to the question of mere perseverance, there was much that would deter the majority of investigators from undertaking such a work; the quarter of Berlin in which Landolt's institute was situated afforded the freedom from earth-tremors requisite for such delicate weighings only twice in the twenty-four hours: once at noon, and again in the small hours of the morning. To carry out a two-hours' weighing in such circumstances is not a task to be relished.

The work he gave to posterity will remain of monumental importance. It was of no small advantage that the final experiments were carried out, after Landolt's retirement, in the Government technical-physical laboratories of which he was curator. Indeed, another important research was planned in collaboration with Quincke, but this was never put in hand. The minor experiments connected with the indestructibility of matter, which refuted the statement of Zengelis that glass was permeable to iodine and similar substances, completed Landolt's life-work. His last scientific communication was but recently read before the Royal Prussian Academy of Sciences, whilst for the following May he had contemplated writing a comprehensive report on the determination of weight.

Landolt's temperament was a most peculiar one, dominated by a modest and delicate, although irresistible humour. This, which in others is frequently only the result of wide experience in life, was in him certainly innate, for Roscoe described him, as early as the Heidelberg days (1865), as "full of dry humour, aber etwas schweigsam," commending at the same time his good-natured equability in the discussion of scientific matters. This humour was always deep, and could be personal, but never wounded; indeed, Landolt never hesitated to turn the point of his wit against himself, although always with that discrimination which may be regarded as characteristic of him.

Professor Stumpf once described Landolt as "ein Lebensphilosoph," and this is a true characterisation, both in a scientific and a personal sense. Although in neither respect was he spared suffering, he always took the cheerful view of a true philosopher. Fundamentally, his character was serious, yet he knew so well how to take this serious view of life that he rarely appeared grave, and never lost the subtle smile which was one of his leading characteristics, and which won the hearts of all. One might have thought that there was for Landolt but one all-important thing in life: his cigar. The following anecdote, relating to his last years, is told by his widow: The secretary of the Berlin Academy, Professor Diels, not long ago sent to Landolt a birthday greeting, expressing the hope that he might be as fresh on his eightieth birthday as he was then. Landolt went at once to his desk and penned the following reply:

> "Die freundlich gewünschten 80
> Will in Geduld ich erharren,
> Ich hoffe die Sache macht sich
> Vermittels recht vieler Zigarren."

He hoped, indeed, to do many another piece of work, and was also considering Ostwald's suggestion that he should write down reminiscences of his life. It is a pity that he was unable to do

this, for, in view of his constant good humour, his clear and simple conception of life, his kindness and thoughtfulness for others, and his large circle of acquaintances, these would have proved interesting memoirs.

Landolt's was essentially a robust nature. He had lived long, and accomplished much without appreciable disturbance in his health. As recently as last year he was planning with Quincke a research of considerable extent. But after recovering from an attack of pleurisy at Karlsbad, he suffered from shortness of breath. The experiments planned with Quincke were never carried out, as their prospects appeared somewhat uncertain. Landolt soon thereafter made over all his apparatus to his son and to his grandson, and gave up experimental work altogether.

On the afternoon of Monday, March 7th, a week before his death, after Landolt had worked uninterruptedly from half-past nine until two o'clock, he was attacked by a fit of choking, which recurred in the evening. The doctor at once predicted the worst. The painful attacks were repeated; the action of the heart and kidneys failed, poisoning his strong system, which was racked with pain in spite of repeated doses of morphia. These were days of torture and anxiety. He lamented that it should be necessary to go through so much suffering in order to die, but he frequently refused the injection of morphia in order to be able to talk over with his youngest grandson, Erich Liebreich, the unfinished portions of his work. He dictated some sentences; explained in which pigeon-holes of his desk were to be found his manuscript and notes—but soon relapsed into unconsciousness. He died at three o'clock on the morning of March 15th.

Landolt was buried, in accordance with his desire, at Bonn, where he had held his first position as a teacher, and had found his life's companion.

H. T. C.

NIKOLAI ALEXANDROVITSCH MENSCHUTKIN.

BORN OCTOBER 25TH, 1842; DIED FEBRUARY 5TH, 1907.

THE year 1907 will ever be memorable in the annals of chemistry on account of the losses, by the hand of death, in the ranks of our leaders: first, within three days of each other, Mendeléeff and Menschutkin in Russia, and only a few weeks later in France, Moissan and Berthelot.

The name of Menschutkin was familiar enough in England, and his services to science, principally in the domain of physico-organic chemistry, were recognised by the Chemical Society in 1898, when

it was added to the limited list of Honorary and Foreign Members, but his figure was less known in this country than that of his great contemporary Mendeléeff. He was, however, present at the famous meeting of the British Association in Manchester in 1887.

The story of Menschutkin's life has been written by his son and successor in the Polytechnic Institute of St. Petersburg-Sosnowka, Professor Boris N. Menschutkin. Unfortunately, it appears in the Journal of the Russian Chemical Society only in the Russian language, and is therefore inaccessible to the majority of chemists, but the facts relating to the greater part of Menschutkin's scientific work are available for English readers through the medium of the abstracts which have appeared since 1871 in the Journal of the Chemical Society. His book on analytical chemistry has also been extensively used in England and America in the form of the English translation by James Locke.

*Nikolai Alexandrovitsch Menschutkin was the sixth son of his father, Alexander Nikolaevitsch Menschutkin, a member of a family, chiefly of merchants, long established in St. Petersburg. His education was received, first at the Gymnasium, which he left, in December, 1857, with the highest distinction, in order to proceed to the University. As he was still under the prescribed age of sixteen years, it was only in the autumn of 1858, and then by special favour, that he was able to enter as a student in the natural science division of the Physico-mathematical Faculty of the University. During three years he worked diligently until, in the autumn of 1861, he experienced, for the first but not the only time, the effects of the operation of those administrative agencies which are the bane of intellectual life in Russia. In consequence of some disturbance among the students, probably of a political character but also probably of no importance, Menschutkin and thirty-one other students were "sent down."

However, in the spring of the following year he succeeded in passing the final examination, and attained the degree equivalent to Ph.D. During the latter part of his course his attention was specially directed to chemistry, which he studied under Professors Woskressenski, Mendeléeff, and Sokoloff. He thus acquired a sufficient knowledge of theory, but he was unable to work practically, as at that time the entire laboratory of the University consisted of only two small rooms. In order to obtain the necessary practice he therefore had to go abroad, and in the following three years he spent two semesters with Strecker in Tübingen, a

* The writer is indebted for the facts narrated in the following account to the notice which appears in *Ber.*, 1907, **40**, 5087

year (1864–5) with A. Wurtz in Paris, and a semester in the laboratory of Kolbe in Marburg.

In the meantime, many changes were introduced into the constitution of the Russian universities. In 1863 the universities obtained academic freedom, they chose for themselves the professors, deans, and rectors, at the same time the number of professors was increased, the means of teaching improved, and, especially owing to Mendeléeff's efforts, the laboratory at St. Petersburg was enlarged.

In 1865 Menschutkin's return to St. Petersburg prevented his dissertation, which had already appeared in the *Comptes Rendus* of the French Academy under the title "Action du chlorure d'acétyle sur l'acide phosphoreux," and in March, 1866, obtained the degree of Master in Chemistry, together with the "venia legendi." Thereupon he began in the autumn a course of lectures on organic nitrogen compounds, and worked at his dissertation for the Doctorate. Having been appointed "Docent" in Analytical Chemistry, he began, in the enlarged laboratory, the course of instruction in that subject which he continued to direct for seventeen years down to 1885.

Early in 1869 the dissertation was ready, the subject being "The Synthesis and Properties of the Ureides," and on the 6th April Menschutkin become Doctor in Chemistry, and thereby eligible for a professorship.

At that time the two chairs of pure chemistry and organic chemistry were occupied by Mendeléeff and Butleroff respectively. The third, relating to technical chemistry, was unoccupied, and in the exercise of the powers recently conferred by the Government, the University Council decided to associate the vacant post with analytical chemistry. Menschutkin was appointed, and although officially Professor of Technical Chemistry he was actually Professor of Analytical Chemistry. In connexion with his teaching he then proceeded to rearrange the course of instruction, and in 1871 he brought out his well-known text-book. This has passed through nine editions, and has been translated into German and English. This work is well and clearly written, and although it contains nothing new in the methods of analysis described, the course represented is an excellent one for students. The author's views as to the place of analytical chemistry in the curriculum, and its relations to other departments of scientific chemistry, are set forth in the preface, from which the following extract will be sufficient. He says: "The student cannot rightly turn to analytical chemistry until he has obtained a thorough preparation in the general science; and his knowledge of the latter is measured

not by the number of single and isolated facts with which he is familiar, but by the clearness with which he understands the fundamental chemical phenomena and theories. For these reasons I strongly advise the beginner not to devote himself too quickly to analytical chemistry. . . . If the above conclusions are correct, the practice of chemical analysis must be pursued in the same way as purely scientific investigations. The chemist proves the correctness of an induction in the latter by means of suitable experiment, in obtaining the best possible conditions for which he must be governed by analogy. The same method of procedure should be adopted by the analytical student, in continually proposing questions to himself and answering them by properly selected experiments." With these remarks most experienced teachers will be in hearty agreement.

In the year 1871 Menschutkin became Secretary of the Physico-mathematical Faculty, and in 1879 he was appointed Dean, an office which he held until 1887.

The assassination of the Emperor Alexander II. in 1881 was followed by the adoption of severe repressive measures, from the effects of which the universities, with all the other institutions in the country, suffered in many ways. The autonomy granted in 1863 was revoked, and the officials, including professors, could only be appointed by the Minister of Public Instruction, the students were required to resume the uniform of 1835, the admission of students rendered much more difficult, as they could only be received from certain gymnasia, the fees were raised considerably, and the number of professorships reduced. In chemistry two only remained, namely, the chairs of pure and technical chemistry.

Naturally, professors and students alike were discontented with this state of things, and in the years 1887–8 serious disturbances occurred. These were followed by the resignation of the rector and several other officials. Butleroff having resigned his post in 1885, Menschutkin had to take up the teaching of organic chemistry, in addition to his other duties. About this time he prepared his large handbook of organic chemistry, which appeared in three successive editions, and in 1888 he published a history of the development of chemical theory. As both these books were written in the Russian language and were not translated into any other, they remain practically unknown to foreigners.

One of Menschutkin's most serious undertakings was the building of the new chemical laboratories of the University. Although the old laboratory had been from time to time enlarged, it was very inconvenient and dark. As it was also far too small for the

number of students desiring admission, a new laboratory was granted on the petition of Mendeléeff and Menschutkin. It was, however, only in 1890 that the money could be found and the plans prepared, and in this year Mendeléeff resigned his chair. This retirement left Menschutkin in the position of senior Professor and Chairman of the Building Committee. After visiting, in company with the architect, Krassowski, several of the chief continental laboratories, Menschutkin returned to St. Petersburg, and the work proceeded so rapidly that the new laboratory was ready for occupation in October, 1894.

In this laboratory Menschutkin worked eight years, teaching only organic chemistry. The later years, however, from 1899 onward, were much disturbed owing to frequent disorders among the students, in consequence of which, from 1899 to 1906, the lecture courses were never completed. In 1902 Menschutkin was transferred to the new Polytechnic Institute, about 6 kilometres north of St. Petersburg, in the district Sosnowka, while still retaining the Professorship of Organic Chemistry in the University, and delivering lectures in that subject. Here he exercised the functions of Professor of Analytical and Organic Chemistry, as well as Dean of the Mining Division. To these offices were added the business connected with the Russian Chemical Society, of which Menschutkin had been Secretary from the commencement down to 1891, and of which he continued to hold the Editorship of the Journal until 1901. In 1906 he was elected President of the Society.

Nor was his activity confined to academic spheres. As deputy of a province he was able to take part in the discussion of questions relating to popular education, and many new schools owe their existence to his exertions. He was also President of the Committee on the establishment of an Agricultural Institute at St. Petersburg.

In his political views he belonged to the Opposition. He often visited the University during the periods of most severe reaction, and in the Council of the Polytechnic he was bold enough to express the view that academic life could only develop under the condition of civil political freedom, and succeeded in carrying a resolution to that effect. He was one of the founders of the Academic League (Bund), and at the end of 1905 he took an active part in the elections for the first Duma. He was one of the founders of the party of democratic reform.

Menschutkin had suffered for many years from disorder of the kidneys, and at the end of 1906 he had an attack which, however, had apparently passed off. His death, which occurred in

the early morning of the 5th February, 1907, was sudden and unexpected.

As to Menschutkin's scientific work, his earliest efforts have been already mentioned. His principal systematic researches relate exclusively to the study of organic compounds from the physical point of view. His important memoirs on the influence of isomerism among alcohols and acids on esterification may be read in full abstract in the *Berichte D. Chem. Ges.* (Bd. 10, 11, 13, 14, 15, 16). Many years earlier it had already been shown by Berthelot and Péan de St. Gilles that in the interaction of acids and primary alcohols there is a limit, both to the rate of change and the amount of ester formed. These researches belong, however, to a time before the complete recognition of isomerism among the alcohols. Menschutkin, in a long series of experiments, showed that, both in respect of rate and limit, the primary, secondary, and tertiary alcohols differ from one another, and that unsaturated differ from saturated alcohols. The molecular weight of the alcohol concerned has also a considerable influence on the result, the limit rising generally with molecular weight, although the rate is diminished. The first series of experiments were made with acetic acid and various alcohols; the succeeding memoirs included the results of work with a variety of acids. Subsequently the rate of chemical change was studied in the case of the formation of amides and anilides by the action of ammonia and aniline on acids by means of the same method as was employed in the esterification experiments. Here again the influence of isomeric differences was equally manifest. These researches led on to others, such as the study of the mutual displacement of bases in homogeneous systems, and the influence of temperature on the rate of several reactions. Abstracts of all the memoirs relating to these researches are provided in the Journal of the Chemical Society.

Menschutkin's researches, from 1889 to 1895, were devoted to the study chiefly of the amines and of the velocity of their interaction with alkyl halogen compounds, and the influence of isomerism on the rate of change. In this connexion the interesting fact was discovered that so-called "indifferent" solvents exercise a quite extraordinary influence on the rate of the reaction.

Continuing these investigations down to the end of his life, Menschutkin succeeded in establishing a large number of other facts connecting together constitution or structure and chemical activity, as well as physical properties, such as boiling point, melting point, and specific gravity. He must, in fact, be regarded as one of the chief pioneers in the difficult study of chemical

dynamics, for although Berthelot had been before him in observations of the rate of esterification, and Harcourt and Esson, in 1864, had made a bold beginning in another direction, the material requisite for generalisation was wanting until much of it was supplied by the continuous, steadfast, and careful researches of the Russian chemist.

In reviewing the career of a great man, interest and sympathy are roused as much by a consideration of the difficulties he has had to encounter and the influence they may be supposed to have had on his character, and the position he ultimately reached, as by any record of his successes or times of triumph. In many cases, these difficulties occurs in early life, and among the worst may be reckoned poverty, ill-health, want of education, or want of friends. These are disadvantages which may beset the youth of any nation, although it may sometimes be said that there are uses in such adversity,

> "Which, like the toad, ugly and venomous,
> Wears yet a precious jewel in his head."

The difficulties which haunt the Russian man of science are not specially of this kind; they do not belong to his youth only or to the circumstances surrounding him individually. They follow him through life, they belong to the atmosphere in which he draws his breath, and over which he has usually no power or control. Those who live under other skies cannot but look wistfully across the frontier of this great country with sympathy in their hearts, and with admiration for those who, like Menschutkin, have succeeded, in the face of disturbance and of official discouragement, in bearing a distinguished part in building the foundations of modern science.

W. A. T.

SIR WALTER PALMER, Bart.

BORN FEBRUARY 4TH, 1858; DIED APRIL 16TH, 1910.

By the death of Sir Walter Palmer we have lost one of the men whose value to the nation we are beginning to appreciate. As the third son of the late George Palmer, M.P. for Reading, the founder of the firm known all over the world as Messrs. Huntley and Palmers, he was one of the directors of a great commercial organisation. Owing to his father's foresight, and to his own natural bent, he received a thorough scientific education that enabled him to take his place on the board of directors as their natural scientific advisor, and out of the happy combination of commercial and scientific experience he developed an attitude of mind towards industrial problems and the scientific principles upon which modern industry must lean that made him an admirable example of the broad-minded captain of industry.

By inheritance and by the education of childhood and boyhood he was excellently endowed from the first. Issued, both on his father's side and on his mother's, from a long and healthy line of forbears belonging to the Society of Friends, his first education was sound and good. And, as a natural part of that education, he made early acquaintance with the outer world by travel and by the study of foreign languages. He matriculated at the age of seventeen at the University of London, and after three years of further study at University College and at the Sorbonne in Paris, he took his B.Sc.Lond., chemistry having been the subject to which he had devoted most attention.

He was now ready to enter upon the practical business of life, and went into the biscuit factory at Reading to serve as a "hand" in its various departments as the proper introduction to his service as a partner in the control and direction of the business.

In that capacity he worked actively for years, and applied his scientific knowledge and method to the technical improvement of biscuit-baking. He thus contributed largely to the commercial prosperity of the firm. As one step towards that end he was chiefly instrumental in the establishment of a chemical laboratory under the direction of a first-rate scientific chemist.

By his marriage in 1882 to Jean, daughter of W. T. Craig, M.P., Walter Palmer's natural disposition to take part in public life, and his natural taste for the literary and artistic aspects, were most happily seconded, and throughout their married life of twenty-seven years the natural generosity of husband and

wife were united, to the great benefit of many artists, and to the great enjoyment of a large circle of friends, both in Reading and in London.

In 1892 Walter Palmer took a leading part in the foundation of the University College of Reading, of which he was the first chairman, and of which the buildings were formally opened in 1898 by H.R.H. the Prince of Wales (King Edward VII.).

In 1891 he generously supported a scheme for the regular delivery of post-graduate lectures in physiology at the University of London, and provided funds for the equipment of the laboratory that was required for this purpose.

In 1898 he was returned to Parliament as the Unionist Member for the City of Salisbury. In 1904 he was created a baronet, and during the last few years until his death he served regularly as a member of the Senate of the University of London.

A. D. W.

CLXXXVII.—*The System: Palmitic Acid–Sodium Palmitate.*

By Frederick George Donnan and Albert Simpson White.

As a substance of very great commercial importance, soap claims a large share of attention from both the industrial and the academic chemist. Although the fundamental reaction—the saponification of an ester—is simple, and has been familiar for a great many years, there are processes in the manufacture of soaps, such as clear-boiling, salting out, etc., which are little understood from a scientific point of view.

Several papers have been published dealing with the condition of soaps in solution in various solvents, especially water (Krafft and collaborators, *Ber.*, 1894, **27**, 1747, 1755; 1895, **28**, 2573; 1896, **29**, 1328, 1334; Kahlenberg and Schreiner, *Zeitsch. physikal. Chem.*, 1898, **27**, 552; A. Smits, *ibid.*, 1903, **45**, 608; McBain and Taylor, *Ber.*, 1910, **43**, 321; *Zeitsch. physikal. Chem.*, 1911, **76**, 2, 179).

The conclusion was arrived at by Krafft that the formation of acid salts played no unimportant part in the chemistry of the soaps, and it was thought that an examination of the two-component system, fatty acid–sodium salt, would possibly afford confirmation of this view, and lead to the isolation of one or more acid salts.

Some preliminary measurements of the "initial freezing points" (called in future I.F.P.'s) of various mixtures of palmitic acid and

sodium palmitate had already been made in this laboratory by H. E. Potts, the results of which are given in the following table.

TABLE I.

No.	Sodium palmitate, per cent.	I.F.P.	No.	Sodium palmitate, per cent.	I.F.P.
1	0	60·65°	8	5	64·00°
2	1	60·50	9	10	66·50
3	2	60·15	10	15	68·60
4	3	60·00	11	20	70·70
5	4	60·70	12	30	75·80
6	5	61·60	13	40	88·70
7	10	65·20			

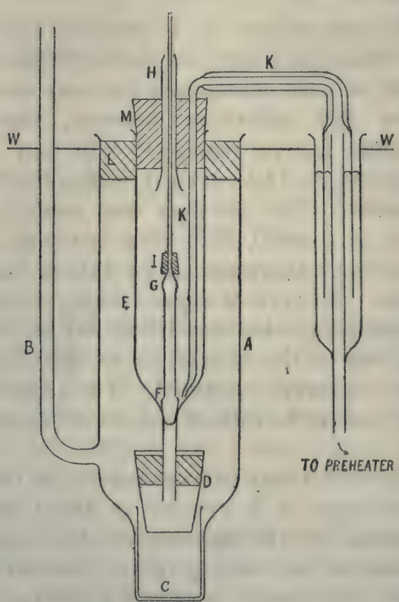
The results of experiments 1—7 were obtained by means of cooling curves. These gave very satisfactory figures when working with the pure acid, or with mixtures of low soap-content. At higher concentrations of the palmitate, however, they became very indefinite, and could not be repeated with any accuracy. The results of experiments 8—13 in table I. were obtained by a method of direct observation. The mixture was made up, melted, and thoroughly mixed, in a small, thin glass test-tube, which was then secured to the bulb of a thermometer by rubber bands, and dipped into a cooling bath. To prevent super-cooling, a stirrer of platinum wire was introduced, and this was lifted out at short intervals in order to allow a drop of the mixture to solidify on it, when it was re-introduced and vigorously agitated. The temperature at which a solid phase was seen to be formed was noted as the I.F.P. of that mixture.

Although no great accuracy can be claimed for these results, they show unmistakable signs of a eutectic at about 60°—a deduction which is corroborated by the appearance of a second halt at this temperature in some of the cooling curves. An attempt to redetermine these points with greater accuracy proved of no avail, as it was found that the mixtures had a very pronounced tendency to supercool, and that crystallisation was very slow, even when started. The viscosity also increases greatly with the addition of soap to the mixtures, at about 35 or 40 per cent. of sodium palmitate being very pronounced. Therefore, as these determinations of I.F.P.'s did not yield the data required with reference to the solid phases, no further time was spent on this work, but the isolation and examination of the solid and liquid phases in equilibrium with each other at various temperatures were proceeded with, the I.F.P. curve being used as a guide in fixing the temperatures and compositions to be used.

Apparatus.

The apparatus used in these solubility determinations consisted essentially of two parts, namely, an inner chamber where equilibrium was attained, and an outer case, for purposes of isothermal filtration. The whole is shown in Fig. 1, in which *A* is the outer case, which was plunged into a thermostat up to the level *WW*. A side-tube *B* led out of the thermostat to the filter pump, and the lower end of *A* was narrowed to accommodate a weighing bottle *C*, in which the liquid phase collected as it fell from a Gooch crucible

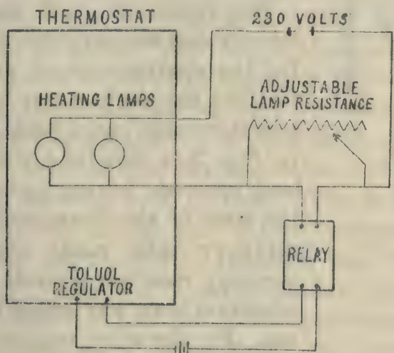
FIG. 1.



D, after having passed through a filter paper. *A* was closed at the top by a large cork, which was bored to support the equilibrium tube *E*, and was rendered air-tight by being covered with a layer of "plasticine," a patent modelling clay which was found very useful for such purposes. *E* was made of one-inch glass tube, narrowed off at the bottom, and sealed into a piece of narrow glass tube which passed through a rubber bung supporting *D*. Communication between *E* and *D* was cut off by means of a ground-glass plug *F*, the stem of which was enlarged into a small bulb *G*, and then drawn out on the upper side, in order to pass easily through the tube *H*, leaving a free air-outlet. A small cork *I* was

dropped on to G, the bottom end of H being enlarged to fit this cork, and so provide a means of supporting the stopper when lifted in order to allow the contents of E to flow down for filtration. The stirring was performed by means of a current of dry air, free from carbon dioxide, which was drawn through the mixture. This was admitted through a narrow glass tube K, drawn off to a fine jet at the lower end, and sucked out through H, which was connected to the filter pump. The end of the stem of F was cut off, so that when in position as shown in Fig. 1 there was a sufficient length projecting to afford a good hold for the fingers, and at the same time not too much to prevent a piece of pressure tubing being slipped over H without danger of breakage. When the stopper was raised for filtration it was no longer necessary to suck air out through H, which was then simply closed up by means of an

Fig. 2.

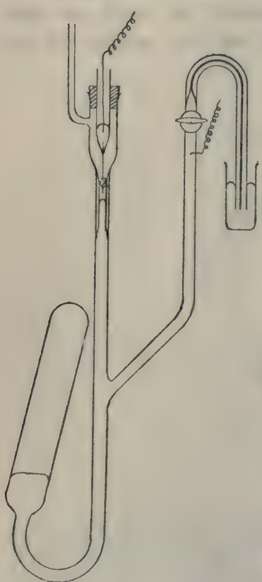


air-tight cap made of rubber tubing long enough to cover the stem in its new position. By this method air was prevented from entering the apparatus through H during filtration. Connexion between the equilibrium apparatus and the preheater—a thin glass spiral immersed in the thermostat, through which the air was passed after purification and before entering the apparatus—was made through mercury, so that the whole apparatus could be lifted easily, without damage to the fragile preheater, which was permanently mounted in the bath. The part of the inlet-tube K which projected out of the thermostat was made of thick-walled glass to minimise the temperature fall which must occur here.

As, at the temperatures required, gas-heated thermostats have been found to be not very satisfactory, the bath used in this work was heated and controlled by electricity, and is perhaps worthy of a short description. Fig. 2 shows the connexions diagrammati-

cally. The heating lamps—two or three 250-watt radiator lamps, according to the temperature—were connected across the 230-volt mains through a relay, across the same terminals of which was also an external adjustable resistance of lamps. This arrangement had a two-fold advantage, since, besides reducing the sparking in the relay, it allowed the rate of cooling of the bath to be regulated. When the direct passage through the relay was broken, the current still had a path through this adjustable resistance in series with the heating lamps, which were thus always absorbing a certain amount of power. This point is of importance, as, at such high temperatures, if the lamps are allowed to be quite extinguished, the cooling is so rapid that the fall of temperature cannot make itself readily enough felt through the walls of the regulator, and bad regulation results.

FIG. 3.



The regulator used was an ordinary toluene and mercury one, but was modified for the electric control, and also in order to allow the temperature to be varied over a considerable range with ease. As shown in Fig. 3, a side-tube was sealed on and bent upwards, having a glass tap just above the level of the thermostat. Above this a capillary tube made connexion with a mercury reservoir outside the bath, and a platinum wire was sealed in just below the tap. For the other contact a piece of stout platinum wire was sealed through the bottom of a narrow glass tube containing a little mercury, into which a copper wire could be dipped. This tube was passed through a cork which fitted the enlarged top of the straight limb of the regulator, and the end of the platinum wire entered a piece of capillary tubing, being bent into the form of a spiral with a central point projecting downwards, in order to keep the contact between platinum and mercury rigidly in the centre of the capillary. To regulate to any desired temperature, mercury was poured into the straight limb until it began to flow over into the reservoir. It now syphoned over until the levels in the capillary and the reservoir were equal, and was ready for use. The detachable contact was put into place, and the bath heated up with the tap open until the temperature was approximately reached. The reservoir was now raised until the meniscus in the capillary was

nearly in contact with the platinum point, and the tap was closed.

If the temperature attained was not quite that required, the final adjustment was made by opening the tap, and either blowing or sucking down a side-tube sealed in to the straight limb for this purpose, and not by alteration of the position of the platinum contact, which was only made detachable for cleaning purposes. The regulator circuit was operated by an accumulator giving approximately 2 volts.

Experimental Results.

Using the I.F.P. curve as a guide, a mixture and temperature were selected which would, in all probability, give both phases in quantities sufficient for analytical purposes. This mixture was made up on a watch glass, and brushed into the apparatus. The cork *I* was then dropped into place, and the apparatus closed up by the rubber bung carrying *H* and *K*, which was pressed down firmly until quite air-tight. The temperature of the bath was adjusted, and if it was required to approach the equilibrium from the solid side the apparatus was at once put into the thermostat. In this case stirring was not started at once, as the powdery mixture would have been blown all over the apparatus. Sufficient time was therefore allowed for the acid to melt. The tube *H* was then connected to the filter pump, and a slow current of air drawn through. When it was desired to approach the equilibrium from the completely liquid side, the mixture was first melted by heating the apparatus in water until all the sodium palmitate had dissolved, and stirring was commenced immediately on transference to the bath. After having been maintained at this temperature for the desired length of time, the apparatus was lifted out and examined, to make sure that both phases were present in sufficient quantities. This could be done very easily and rapidly without fear of disturbing the equilibrium, as the whole apparatus was mounted on a single support, and was connected with the preheater through mercury, as mentioned previously. If the result of this examination was unsatisfactory, the apparatus was replaced, and the temperature altered in the required direction, and a further period allowed. If, however, both phases were present as desired, the apparatus was replaced quickly, and a short time allowed to neutralise the effect of the small amount of cooling that had taken place. The stopper was then raised, and *H* closed up as described, and the outlet tube *B* connected with the pump, thus sucking air through the solid phase collected in *D*, and allowing the liquid phase to fall into *C*. The phases so collected were then taken out,

and their sodium content estimated as sulphate, after careful ignition to drive off all the organic matter.

In order to gain a knowledge of the time necessary for the establishment of equilibrium, the following experiments were carried out at 60°.

TABLE II.

Condition of mixture before experiment.	Time in days.	Solid phase, sodium palmitate, per cent.	Liquid phase, sodium palmitate, per cent.
Liquid	2	22·84	19·1
,, ...	2	22·84	19·22
Solid	2	22·95	19·1
,, ...	2½	22·84	19·33
Liquid	2½	22·72	19·1

From table II. equilibrium is seen to be sufficiently attained in two days, and as this was a convenient time, no further work was done on this question, but in the following experiments a period of at least two days was allowed for the attainment of equilibrium.

Table III. gives the results obtained, both in percentages of sodium and of sodium palmitate.

TABLE III.

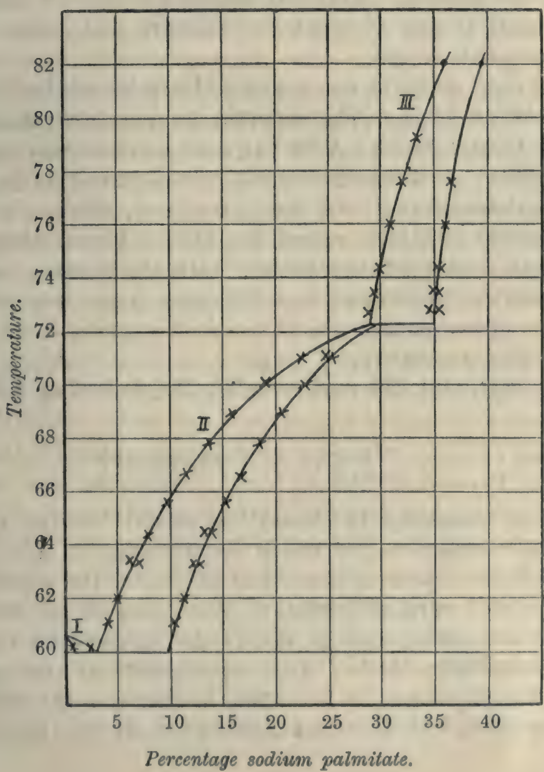
		Solid phase.		Liquid phase.	
No.	Temp.	Per cent. Na.	Per cent. NaPa.	Per cent. Na.	Per cent. NaPa.
1	60·2°	0·06	0·7	0·19	2·3
1	60·2	0·05	0·6	0·19	2·3
2	61·1	0·84	10·20	0·32	3·97
2	61·1	0·85	10·30	0·34	4·17
3	62·0	0·92	11·12	0·41	4·96
3	62·0	0·93	11·34	0·41	4·96
4	63·3	1·02	12·33	0·54	6·53
4	63·3	1·06	12·81	0·52	6·28
5	64·4	1·14	13·78	0·66	7·98
5	64·4	1·12	13·54	—	—
6	65·6	1·28	15·47	0·82	9·91
6	65·6	—	—	0·82	9·91
7	66·65	1·38	16·68	0·95	11·48
7	66·65	1·32	15·95	1·00	12·09
8	67·75	1·55	18·73	1·12	13·54
8	67·75	1·545	18·67	1·15	13·90
9	68·95	1·70	20·55	1·37	15·56
9	68·95	1·71	20·67	—	—
10	70·00	1·89	22·84	1·59	19·22
10	70·00	1·89	22·84	1·58	19·10
11	71·00	2·10	25·38	1·87	22·60
11	71·00	2·07	25·02	1·87	22·60
12	72·9	2·90	35·05	2·37	28·65
12	72·9	2·85	34·45	2·36	28·52
13	73·5	2·65	32·39	2·42	29·25
13	73·5	2·68	32·03	2·43	29·37
14	73·5	2·90	35·05	2·39	28·89
14	73·5	2·93	35·41	2·37	28·65

TABLE III (*continued*).

		Solid phase.		Liquid phase.	
No.	Temp.	Per cent. Na.	Per cent. NaPa.	Per cent. Na.	Per cent. NaPa.
15	74·4	2·93	35·41	2·48	29·98
15	74·4	2·91	35·17	2·48	29·98
16	76·0	2·97	35·90	2·54	30·70
16	76·0	3·00	36·26	2·53	30·58
17	77·6	3·02	36·50	2·65	32·03
17	77·6	—	—	2·65	32·03
18	79·2	2·95	35·66	2·76	33·36
18	79·2	3·00	36·26	—	—
19	82·0	3·28	39·64	2·98	36·02
19	82·0	—	—	2·97	35·90

The above results are shown graphically in Fig. 4. They are seen to form three pairs of curves, indicating the formation of three

FIG. 4.



series of solid solutions. The lower eutectic was already fixed by the second halt noticed by Potts in his cooling curves. The second pair of curves appears to approach a maximum so nearly, before the second eutectic is reached, that further experiment was required to settle this point. An attempt was made to fix this second eutectic temperature also by means of cooling curves, but without result, on account of the supercooling and slow velocity of crystallisation mentioned before. The difficulty of obtaining definite results from cooling curves was found to increase rapidly with the addition of sodium palmitate to the mixtures, and with the compositions required for the present purpose the method was quite useless. The following two methods of obtaining the eutectic temperature by melting a mixture were therefore tried.

A mixture containing 29 per cent. of sodium palmitate and 71 per cent. of palmitic acid was melted and thoroughly mixed in a test-tube, and then cooled quickly. It was then allowed to remain in the thermostat for some time, after which it was examined, and its condition noted. The temperature was then raised slightly, and a further time allowed. This was repeated until two temperatures were obtained, at one of which the mixture was quite solid, and at the other partly liquid.

A 29 per cent. mixture was found to be quite solid at 72·1°, and partly liquid at 72·6°. The eutectic temperature therefore lies between 72·1° and 72·6°. A 29 per cent. mixture was again made up, and melted. A thermometer was stirred round in the liquid to ensure complete mixing, and then lifted out, when a film of the mixture quickly solidified round the bulb. It was then enclosed in an air-bath, and gradually heated, until the mixture was noticed to flow down the thermometer and form a large drop on the end of the bulb. The temperature at which this occurred was accepted as the eutectic temperature.

Working with two different samples, the following results were obtained:

Experiment 1	72·4°	Experiment 2	72·3°
,, 1*a*	72·3	,, 2*a*	72·4

It was now necessary to obtain the initial freezing point of a mixture, the composition of which lies between 29 per cent. and that of the highest pair of analytical points on the second pair of curves. For this purpose a mixture containing 26 per cent. of the sodium salt was taken, that is, nearly the composition represented by the formula NaPa,3HPa. This experiment was also carried out by coating the thermometer bulb, but in this case the temperature accepted as the I.F.P. (or final melting point) was that at which

the drop on the end of the thermometer became quite transparent. The experiments gave the results:

Experiment	1	71·8°
,,	2	71·7
,,	3	71·8

These results, when plotted in Fig. 4, are seen to agree very well with the analytical results, and practically to exclude the existence of a stable maximum in the second pair of curves before the second eutectic is reached.

The results given in table III., and plotted in Fig. 4, are liable to two sources of inaccuracy, namely, (1) analytical errors, and (2) divergence from the true composition of the solid phase by reason of adhering liquid.

The analytical error is insignificant for the purpose of the present work, the analyses being carried out in duplicate with reasonable agreement.

The second source of error is of greater importance, as one is entirely dependent on the results of analysis in fixing the composition of the solid phase. It might be argued that a solid phase of constant composition corresponding with each branch of the liquid phase curve really separates out, but that this is not recognised owing to incomplete separation from the mother liquor. This view can, however, be shown to be untenable by the following reasoning. Confining one's attention, in the first place, to the middle pair of curves (numbered II. on the diagram), let it be supposed that the true solid phase is one of constant composition, represented by some vertical line on the diagram. Then it must fulfil the condition that this vertical line cannot enter the space enclosed by the analytical curves, as, at the temperatures at which this occurred, a negative amount of wetting would have taken place. It can therefore only cut the solid and liquid phase curves at the point at which they touch each other. One can now assign a simple molecular composition to this constant solid phase, and calculate, or read off from the diagram, the amounts of liquid phase which would have to be associated with unit amount of this, in order to give the analytical results. If this composition corresponding with the second pair of curves be supposed to be that of the possible acid salt NaPa,3HPa (approximately 26 per cent. of sodium palmitate), the solid separated would have to be made up of about one part of the true solid phase and two parts of the liquid phase, a conclusion which is quite absurd. Any assumed composition lying to the right of this on the diagram would, of course, give even more unlikely results,

whilst no simple composition lying to the left exists which does not cut both curves in separate and well-substantiated points.

The same reasoning may be applied to the other pairs of curves. Thus if the solid phase separating along the pair of curves numbered I. were the pure acid, this would have to be associated with about half its weight of liquid phase. The mixtures are here, however, not very viscous, and it is unlikely that such extensive wetting occurs. Along the pair of curves numbered III. the solid phase which suggests itself is the acid salt NaPa,HPa, which, however, contains more than 50 per cent. of the sodium salt, and would have to have been wetted with twice its weight of mother liquor to give the results obtained. In support of the above argument it may also be said that if a composition and temperature were so selected as to be represented by a point lying midway between the liquidus and solidus curves, a practically 50 per cent. mixture of solid and liquid was obtained, although no exact quantitative test of this could be carried out owing to loss on the glass of the apparatus.

The solid phase curve in the third branch undoubtedly suffers more from this wetting than in the other two branches, as the liquid phase is here much more viscous. Indeed, in order to effect a separation at all, matters had to be so arranged that there was much more liquid than solid present, otherwise the material would not flow down into the Gooch crucible. Two experiments are quoted (expts. 13 and 18) in table III. in which this precaution had not been taken. A little liquid phase was separated, and analysed, giving results which fell on the curve, but the solid, when removed from the apparatus, gave points which were well within the area enclosed by the liquidus and solidus curves.

It results from these experiments that no constant solid phases corresponding with acid salts in which the molar ratio $\frac{\text{acid}}{\text{salt}} > 1$ separate out, whilst the separation of the acid salt NaPa,HPa is extremely doubtful, although this composition has not been covered by the experimental data.

The existence of the solid solutions which have been shown to occur is rendered very probable when we consider that the chemical "polarity" between palmitic acid and its sodium salt is relatively small owing to the extent of the carbon chain present in each case. This confers on both acid and salt such a predominating hydrocarbon character that the chemical polarity due to the different residual affinities of the $\cdot CO_2H$ and $\cdot CO_2Na$ groups is to a great extent obliterated. In confirmation of this view may be mentioned the fact that liquid mixtures of palmitic acid and

sodium palmitate show no trace of electrolytic dissociation, the liquid being practically a non-conductor of electricity.

The existence of solid solutions is of considerable interest and importance in relation to the nature of the phases which can separate from aqueous soap solutions, or which are present in the colloidal state in such solutions. It would appear probable that such phases may be simply solid solutions of acid and soap, or else phases, whether liquid or solid, of variable composition, containing the three components, fatty acid, sodium oxide, water.

It is intended to continue this investigation with the object of ascertaining the nature of the phases which can separate from the three-component system, fatty acid, sodium (or potassium) salt, solvent.

Summary of Results.

(1) The two-component system palmitic acid–sodium palmitate has been investigated over a range of compositions extending from the pure acid to a mixture containing about 38 per cent. of the salt, corresponding with the temperature range of 60° to 82°.

(2) The solid phases which separate under these conditions consist of three series of solid solutions.

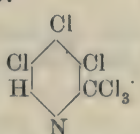
(3) No solid phases corresponding with definite compounds have been found to separate under the conditions of these experiments.

MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,
UNIVERSITY OF LIVERPOOL.

CLXXXVIII.—*The Chlorine Derivatives of Pyridine. Part XI. Some Interactions of* 3 : 4 : 5-*Trichloropicolinic Acid and of its Derivatives.*

By WILLIAM JAMES SELL.

IN former communications (Trans., 1905, **87**, 799; 1908, **93**, 1994) it was shown that one of the chief products of the chlorination of 2-methylpyridine is the compound having the constitution represented by the formula:



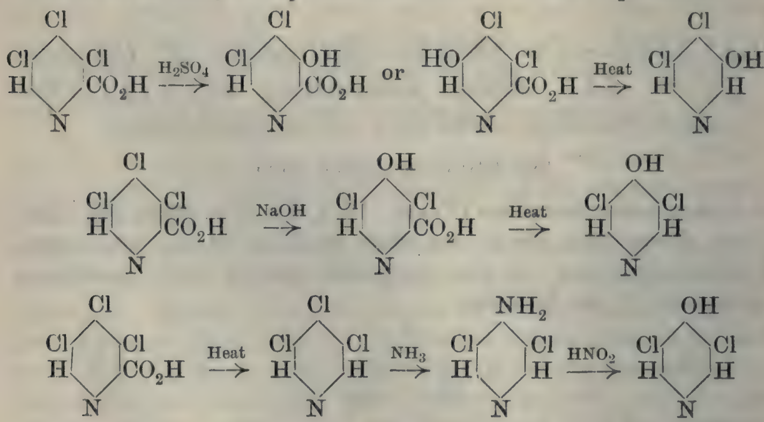
It was further pointed out that this compound undergoes decomposition when heated to 125—130° with 80 per cent. sulphuric

acid, giving mainly 3:4:5-trichloropicolinic acid, but that if the temperature was allowed to rise much above this point part of the acid is resolved into carbon dioxide and 3:4:5-trichloropyridine, which remains dissolved in the sulphuric acid.

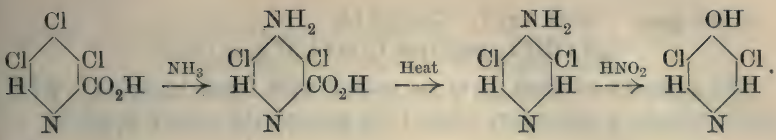
Examination of this decomposition of the hexachloropicoline on a larger scale revealed the fact that in addition to the above products a dichlorohydroxypicolinic acid was also formed in small quantity. This was separated from the later crops of 3:4:5-trichloropicolinic acid by crystallisation from water. The new compound separates from water in colourless, anhydrous needles, and is regarded as having the hydroxyl group in the position 3 or 5. It is resolved by heat without fusion or residue into carbon dioxide and the corresponding dichlorohydroxypyridine, which condenses in the cool part of the tube. An isomeric dichlorohydroxypicolinic acid is obtained from 3:4:5-trichloropicolinic acid by the action of alcoholic sodium hydroxide. The compound is regarded as 3:5-dichloro-4-hydroxypicolinic acid, and is also resolved by heat without fusion or residue into the corresponding dichlorohydroxypyridine * and carbon dioxide.

Further, 3:4:5-trichloropicolinic acid reacts with ammonia when heated in a sealed tube, giving 3:5-dichloro-4-aminopicolinic acid, which on heating gives 3:5-dichloro-4-aminopyridine. The latter compound is converted by nitrosylsulphuric acid into 3:5-dichlorohydroxy-4-pyridine, identical with that obtained by the action of alcoholic sodium hydroxide on 3:4:5-trichloropicolinic acid, and subsequent acidification and heating.

The above changes may for convenience be thus represented:



* This nomenclature is employed for convenience only. The question as to whether this and similar substances are pyridone or hydroxypyridine derivatives is left quite open.



EXPERIMENTAL.

*Formation of Dichloro-*3(or 5)*-hydroxypicolinic Acid from* 3 : 4 : 5*-Trichloropicolinic Acid.*

This compound was separated from the mother liquors in the decomposition of hexachloropicoline by 80 per cent. sulphuric acid, and is doubtless formed from the chief product of this decomposition, namely, 3 : 4 : 5-trichloropicolinic acid, by the displacement of a chlorine atom by an hydroxyl group. The substance separates from water in anhydrous, colourless, microscopic needles, which are moderately soluble in boiling water, sparingly so in cold water, and freely soluble in warm alcohol or ether:

0·124 gave 0·158 CO_2 and 0·0175 H_2O. C = 34·72; H = 1·56.
0·2055 „ 0·2868 AgCl. Cl = 34·50.
0·2053 „ 0·287 AgCl. Cl = 34·58.
$C_6H_3O_3NCl_2$ requires C = 34·61; H = 1·44; Cl = 34·13 per cent.

The compound decomposes without melting, being resolved into 4 : 5-dichloro-3-hydroxypyridine and carbon dioxide. An aqueous solution of the acid gives the following reactions: *Ferric chloride:* a deep brownish-red colour. *Cupric acetate:* bluish-grey, very sparingly soluble, crystalline precipitate. *Silver nitrate:* a gelatinous precipitate, very sparingly soluble in boiling water; the filtered hot liquid deposits needles of the silver salt on cooling.

The ammonium salt of the acid gave with barium chloride a copious precipitate consisting of fine needles.

Calcium chloride gave an immediate precipitate consisting of rosettes of needles, sparingly soluble in boiling water, from which it separates in tufts of silky needles.

Formation of 4 : 5*-Dichloro-3-hydroxypyridine from Dichloro-*3(or 5)*-hydroxypicolinic Acid.*

When the preceding compound is heated in a wide glass tube in a gentle current of air it is resolved without melting or residue into carbon dioxide and 4 : 5-*dichloro-3-hydroxypyridine*, which forms a crystalline sublimate in the cool part of the tube. The sublimate is dissolved in boiling water, and on cooling crystallises in colourless, prismatic needles:

0·143 gave 0·2496 AgCl. Cl = 43·16.

$C_5H_3ONCl_2$ requires Cl = 43·27 per cent.

The aqueous solution gives no colour with ferric chloride. With silver nitrate a granular, crystalline precipitate slowly appears.

Preparation of 3:5-*Dichloro*-4-*hydroxypicolinic Acid from* 3:4:5-*Trichloropicolinic Acid or from Hexachloropicoline.*

When either 3:4:5-trichloropicolinic acid or hexachloropicoline is heated for some hours on the water-bath with excess of alcoholic sodium hydroxide in a flask with reflux, interaction takes place, as shown by the deposit of sodium chloride. The contents of the flask when diluted with water and acidified with hydrogen chloride deposit the acid in creamy-white, globular masses of minute needles, which after washing and recrystallisation from dilute alcohol still remained slightly coloured. The compound does not melt when heated, but is resolved without blackening or residue into carbon dioxide and 3:5-dichloro-4-hydroxypyridine. The substance is but moderately soluble in hot alcohol, acetone, or water, and sparingly so in these solvents in the cold:

0·3935 lost 0·058 H_2O at 144°. H_2O = 14·73.

0·158 gave 0·18662 AgCl. Cl = 29·19.

$C_6H_3O_3NCl_2,2H_2O$ requires H_2O = 14·75; Cl = 29·09 per cent.

A warm saturated aqueous solution of the hydroxy-acid gives the following reactions: *Ferric chloride:* a deep red colour. *Cupric acetate:* a greyish-blue precipitate, consisting of groups of needles. *Silver nitrate:* rosettes of needles on keeping. The ammoniacal solution gave with: *Barium chloride:* a slight crystalline precipitate on keeping. *Calcium chloride:* a precipitate consisting of micaceous plates. *Silver nitrate:* gelatinous, white precipitate, sparingly soluble in boiling water.

Formation of 3:5-*Dichloro*-4-*hydroxypyridine from* 3:5-*Dichloro*-4-*hydroxypicolinic Acid.*

When 3:5-dichloro-4-hydroxypicolinic acid is gradually heated to about 300° it is resolved without previous fusion into carbon dioxide and 3:5-*dichloro*-4-*hydroxypyridine*, the latter condensing in crystals on the cool part of the apparatus. The decomposition may also be brought about by heating in glycerol, but loss of material is occasioned by the difficulty of separating the dichlorohydroxypyridine from the glycerol residue. On recrystallisation from dilute alcohol the substance separates in needles. It is readily soluble in alkalis, and separates on acidification in rosettes of needles:

0·150 gave 0·2606 AgCl. Cl = 42·95.

$C_5H_3ONCl_2$ requires Cl = 43·25 per cent.

An aqueous solution of the compound gives with: *Ferric chloride:* no change of colour. *Silver nitrate:* tufts of needles, slowly precipitated.

The ammoniacal solution gives with: *Barium chloride:* no precipitate, even after keeping. *Calcium chloride:* no precipitate at first, but after some time a crystalline deposit consisting of flat needles and plates.

Conversion of 3:4:5-*Trichloropicolinic Acid into* 3:5-*Dichloro-4-aminopicolinic Acid.*

Five tubes, each containing 2 grams of the acid and 30 c.c. of strong aqueous ammonia, were sealed and heated to 140° for several hours. The product was evaporated to remove the excess of ammonia, the amino-acid precipitated by hydrogen chloride, and after washing purified by crystallisation from water. The substance separates on slow cooling of the hot liquid in massive, prismatic, very faintly coloured crystals containing one molecule of water of crystallisation, and melting and decomposing at 172° (uncorr.):

0·3787 lost 0·0308 H_2O at 100°. H_2O = 8·13.
0·2450 gave 0·286 CO_2 and 0·06 H_2O. C = 31·83; H = 2·71.
0·1713 „ 17·8 c.c. N_2 at 10° and 762 mm. N = 12·47.
0·242 (dried acid) gave 0·3345 AgCl. Cl = 34·172.

$C_6H_4O_2N_2Cl_2,H_2O$ requires H_2O = 8·0; C = 32; H = 2·66; N = 12·44 per cent.

$C_6H_4O_2N_2Cl_2$ requires Cl = 34·29 per cent.

The aqueous solution gives with: *Ferric chloride:* a deep red colour. *Copper acetate:* a light blue, sparingly soluble precipitate consisting of rosettes of minute needles. *Ammoniacal silver nitrate:* a white, gelatinous precipitate, practically insoluble in boiling water. *Barium chloride and ammonia:* a slight, granular precipitate after some time.

Conversion of 3:4:5-*Trichloropyridine into* 3:5-*Dichloro-4-amino-pyridine.*

Trichloropyridine (Trans., 1905, **87**, 802) was heated in a sealed tube with a mixture of equal volumes of strong aqueous ammonia and alcohol for several hours at 150°. The contents of the tube after evaporation to dryness in a vacuum over sulphuric acid were washed with water to remove ammonium chloride, and the residue was crystallised from alcohol. The substance separates from alcohol in long needles, melting at 161° (uncorr.).

The same substance is also readily produced by heating the preceding compound (3:5-dichloro-4-aminopicolinic acid) a few degrees above its melting point, when it is resolved into carbon dioxide and 3:5-*dichloro-4-aminopyridine*. The substance crystallises from alcohol in long needles, melting at 161° (uncorr.):

0·216 gave 31·4 c.c. N_2 at 13° and 752 mm. N = 16·99.
0·086 „ 0·1518 AgCl. Cl = 43·64.
$C_5H_4N_2Cl_2$ requires N = 17·17; Cl = 43·55 per cent.

Conversion of 3:5-*Dichloro-4-aminopyridine into* 3:5-*Dichloro-4-hydroxypyridine.*

A few grams of 3:5-dichloro-4-aminopyridine were dissolved in 80 per cent. sulphuric acid, mixed with an excess of nitrosylsulphuric acid, and heated on the water-bath until no further effervescence was visible. The liquid was poured into cold water, partly neutralised with sodium carbonate, and evaporated to a small bulk. On cooling, the substance separated in needles, and after solution in sodium carbonate and precipitation by dilute sulphuric acid, was crystallised from water, from which it separates in filamentous needles or in rosettes of needles. The qualitative reactions and general characters are identical with those of the substance produced above by other reactions. (Found: Cl = 43·13. Calc., Cl = 43·25 per cent.)

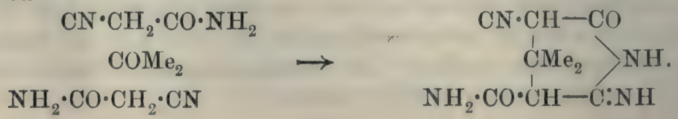
University Laboratory,
Cambridge.

CLXXXIX.—*The Formation and Reactions of Imino-compounds. Part XVI. Reactions Leading to the Formation of Tricarballylic Acid.*

By Ferdinand Bernard Thole and Jocelyn Field Thorpe.

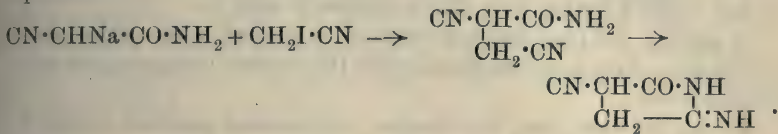
The formation of imino-compounds by the internal coupling of an amino-group, present in an amide, with a nitrile group occupying the δ-position has already been demonstrated by the formation of a series of condensation products from ketones and cyanoacetamide (this vol., p. 422).

Thus it was found that when acetone is condensed with cyano-acetamide in the presence of piperidine the imino-compound is formed:

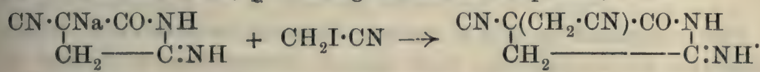


It was therefore to be expected that cyanoamides having the cyano-group in the γ-position would pass into an imino-derivative of the five-membered ring with even greater ease. The present communication deals with two reactions of this type.

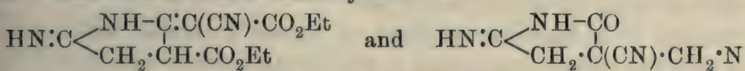
In the first place, it was hoped to prepare a simple compound of this series by the interaction of the sodium compound of cyanoacetamide with iodoacetonitrile in accordance with the equation:



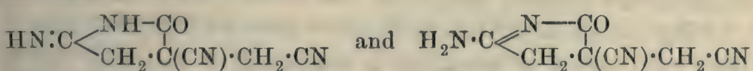
Experiment showed, however, that it was not possible to isolate the condensation product of this formula, because, at the moment of its formation, interaction with unchanged sodiocyanoacetamide ensued, yielding a sodium compound, which then reacted further with iodoacetonitrile, producing an imino-compound, thus:



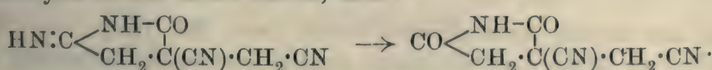
This substance is in many respects analogous to the compound prepared by Best and Thorpe (Trans., 1909, **95**, 1506) by the interaction of the sodium derivative of ethyl β-imino-α-cyanoglutarate and iodoacetonitrile, a relationship which is clearly seen when the two formulæ are written side by side:



In the previous case the compound was shown to react in its tautomeric imino-amino-forms, but to have only a short imino-phase. In the present instance there is no doubt that the imino-compound also reacts in the two forms:



because it not only readily dissolves in dilute hydrochloric acid and is precipitated for the most part unchanged on the addition of sodium acetate, but when the acid solution is warmed, complete hydrolysis to the imide ensues, thus:



The stability of the six-membered ring towards alkali, which was commented on in the previous communication, is also shown by the compound under discussion, for, when it is boiled with alkali hydroxides, it is transformed into the imide of the dicarboxylic

acid, a substance which evolves carbon dioxide on heating, and passes into the imide of tricarballylic acid:

$$\mathrm{HN{:}C}\Big<\begin{array}{l}\mathrm{NH{-}CO}\\ \mathrm{CH_2{\cdot}C(CN){\cdot}CH_2{\cdot}CN}\end{array} \longrightarrow \mathrm{CO}\Big<\begin{array}{l}\mathrm{NH{-}CO}\\ \mathrm{CH_2{\cdot}C(CO_2H){\cdot}CH_2{\cdot}CO_2H}\end{array}$$

$$\longrightarrow \mathrm{CO}\Big<\begin{array}{l}\mathrm{NH{-}CO}\\ \mathrm{CH_2{\cdot}CH{\cdot}CH_2{\cdot}CO_2H}\end{array}.$$

Tricarballylic acid is produced when either the imino-compound or the imide is boiled with dilute sulphuric acid.

A similar five-ring imino-compound is formed when either iodo- or chloro-acetamide is condensed with the sodium compound of ethyl cyanoacetate.

In this reaction, also, the simpler condensation product cannot be isolated, but two molecules of the halogen derivative take part, yielding an imino-compound in accordance with the equation:

$$\mathrm{2CHNa(CN){\cdot}CO_2Et + 2CH_2I{\cdot}CO{\cdot}NH_2} \longrightarrow$$

$$\mathrm{NH_2{\cdot}CO{\cdot}CH_2{\cdot}C(CO_2Et)}\Big<\begin{array}{l}\mathrm{CH_2{-}{-}{-}CO}\\ \mathrm{C({:}NH){\cdot}NH}\end{array} + \mathrm{2NaI + CH_2(CN){\cdot}CO_2Et}.$$

This compound is also a normal imino-amino-derivative, which dissolves unchanged in cold dilute hydrochloric acid, but is hydrolysed on warming to the corresponding imide:

$$\mathrm{NH_2{\cdot}CO{\cdot}CH_2{\cdot}C(CO_2Et)}\Big<\begin{array}{l}\mathrm{CH_2{\cdot}CO}\\ \mathrm{CO{-}{-}NH}\end{array}.$$

Both these compounds yield tricarballylic acid on complete hydrolysis with dilute sulphuric acid.

Finally, it is desirable to place on record a similar experiment in which the sodium compound of ethyl cyanoacetate was condensed with iodoacetonitrile. Here, again, the normal product could not be isolated, and the reaction yielded the trinitrile ester in accordance with the equation:

$$\mathrm{2CHNa(CN){\cdot}CO_2Et + 2CH_2I{\cdot}CN} \longrightarrow$$

$$\mathrm{CH_2(CN){\cdot}C(CN)(CO_2Et){\cdot}CH_2{\cdot}CN + 2NaI + CH_2(CN){\cdot}CO_2Et}.$$

Our main object in preparing a compound of this type was to find if there was any tendency for it to form an imino-compound of the four-membered ring, thus:

$$\mathrm{CO_2Et{\cdot}C(CN)}\Big<\begin{array}{l}\mathrm{CH_2{\cdot}CN}\\ \mathrm{CH_2{\cdot}CN}\end{array} \longrightarrow \mathrm{CO_2Et{\cdot}C(CN)}\Big<\begin{array}{c}\mathrm{CH(CN)}\\ \mathrm{{-}CH_2{-}}\end{array}\Big>\mathrm{C{:}NH}.$$

It has already been shown (Trans., 1908, **93**, 165; 1909, **95**, 1901) that primary nitrile groups readily lead to the formation of imino-derivatives of the five-carbon ring, and therefore a substance of the above formula is admirably suited for the purpose of determining if any tendency exists for the formation of the four-carbon ring in this manner. Previous experiments with glutaronitrile,

$CN\cdot CH_2\cdot CH_2\cdot CH_2\cdot CN$, in this respect had yielded negative results, but the conclusions were not regarded as definite, owing to the very soluble character of the products formed from this nitrile. In the present instance the formation of any imino-compound by the action of sodium ethoxide could have been at once detected, but no such formation occurred.

It is interesting to note that the above nitrile ester can be readily hydrolysed to tricyanohydrin, $CN\cdot CH_2\cdot CH(CN)\cdot CH_2\cdot CN$, a substance which, although it has played an important part in the synthesis of tricarballylic acid from glycerol, does not appear to have been isolated. It is a well defined, crystalline substance, melting at 47°.

Experimental.

2-Imino-4-cyano-4-cyanomethyl-5-pyrrolidone,

$$HN:C<\begin{matrix}NH-CO\\ CH_2\cdot C(CN)\cdot CH_2\cdot CN\end{matrix}$$

This substance is prepared by dissolving 4·6 grams of sodium in 60 c.c. of alcohol, adding 16·8 grams of cyanoacetamide, and then 33 grams of iodoacetonitrile in small portions at a time. The reaction is vigorous, and must be checked by cooling; when finished, the imino-compound separates in the crystalline form when the side of the containing vessel is scratched. It is best purified by dissolving in cold dilute hydrochloric acid, and re-precipitating by the addition of aqueous sodium acetate, but can be obtained crystalline from warm water in small, colourless prisms, which carbonise, without melting, at 215—220°:

0·1715 gave 0·3255 CO_2 and 0·0562 H_2O. C = 51·81; H = 3·62.
0·1058 „ 31·8 c.c. N_2 at 19° and 739 mm. N = 34·4.
$C_7H_6ON_4$ requires C = 51·8; H = 3·7; N = 34·6 per cent.

The imino-compound is soluble in dilute mineral acids, and also dissolves in cold aqueous alkaline hydroxides. It is insoluble in cold solutions of alkali carbonates, and when boiled with water is slowly hydrolysed with evolution of ammonia.

4-Cyano-2:5-diketo-4-cyanomethylpyrrolidine,

$$CO<\begin{matrix}NH-CO\\ CH_2\cdot C(CN)\cdot CH_2\cdot CN\end{matrix}$$

The formation of this substance from the imino-compound may be effected by dissolving the base in dilute hydrochloric acid, and then raising the solution to the boiling point. The imide usually separates completely when the solution is cooled, but if this is not the case it must be isolated by extracting the solution with ether.

It can be purified by crystallisation from water, and obtained in small, colourless prisms, which melt at 137—138°, and blacken at a high temperature:

0·2006 gave 0·3770 CO_2 and 0·0576 H_2O. C = 51·31; H = 3·20.
0·1430 ,, 31·7 c.c. N_2 at 18° and 750 mm. N = 25·8.
$C_7H_5O_2N_3$ requires C = 51·5; H = 3·1; N = 25·8 per cent.

The imide dissolves in aqueous alkali carbonates, and yields a faintly acid solution with water.

The Imide of Tricarballylic Acid,

$$NH<\begin{matrix}CO\cdot CH_2 \\ \quad\; | \\ CO\cdot CH\cdot CH_2\cdot CO_2H.\end{matrix}$$

Five grams of the imino-compound are boiled with excess of potassium hydroxide solution until free from ammonia, when the solution is acidified and extracted with ether. The syrup which remains on evaporating the ether is heated at 180° until all carbon dioxide has been evolved, and the residue is then rubbed with dry ether. The solid obtained in this manner crystallises from benzene in small prisms, melting at 127—128°:

0·1688 gave 0·2844 CO_2 and 0·0673 H_2O. C = 45·94; H = 4·46.
$C_6H_7O_4N$ requires C = 45·9; H = 4·4 per cent.

The imide is readily soluble in water or alcohol, but sparingly so in ether or benzene.

When any one of the above compounds is boiled with dilute sulphuric acid, tricarballylic acid, melting at 165°, is formed. (Found, C = 41·10; H = 4·5. $C_6H_8O_6$ requires C = 40·9; H = 4·5 per cent.) The acid can be obtained from the product of hydrolysis by extraction with ether.

Ethyl 2-Imino-3-carbamylmethyl-5-pyrrolidone-3-carboxylate,

$$NH_2\cdot CO\cdot CH_2\cdot C(CO_2Et)<\begin{matrix}CH_2\text{——}CO \\ \qquad\quad | \\ C(:NH)\cdot NH\end{matrix}.$$

To a solution of 5·8 grams of sodium in 70 c.c. of alcohol, 29 grams of ethyl cyanoacetate are added, and then 23·5 grams of chloroacetamide, the reaction being carried to completion by boiling on the water-bath for one hour. When the solution is evaporated free from most of the alcohol, water precipitates the solid imino-compound, which crystallises from water in voluminous, matted needles, melting at 191° with evolution of gas:

0·1613 gave 0·2806 CO_2 and 0·0817 H_2O. C = 47·41; H = 5·62.
0·1331 ,, 20·9 c.c. N_2 at 18° and 745 mm. N = 18·2.
$C_9H_{13}O_4N_3$ requires C = 47·6; H = 5·7; N = 18·5 per cent.

The imino-compound is readily soluble in dilute hydrochloric acid, and is precipitated, for the most part unchanged, when sodium acetate is added to the solution. It can be recrystallised from alcohol.

Ethyl 2:5-*Diketo-3-carbamylmethylpyrrolidine-3-carboxylate*,

$$NH_2\cdot CO\cdot CH_2\cdot C(CO_2Et){<}\begin{matrix} CH_2\cdot CO \\ | \\ CO\text{--}NH \end{matrix}.$$

The transformation of the imino-compound into this imide can be effected by heating a concentrated solution of it in dilute hydrochloric acid to the boiling point, and allowing the imide to crystallise on cooling. It forms small needles, which melt at 127°:

0·1921 gave 0·3327 CO_2 and 0·0935 H_2O. H=47·23; H=5·41.

$C_9H_{12}O_5N_2$ requires C=47·4; H=5·3 per cent.

The imide is readily soluble in warm water.

Both the above compounds yield tricarballylic acid on complete hydrolysis with dilute sulphuric acid.

Ethyl $\alpha\beta\beta'$-*Tricyano*iso*butyrate*, $CN\cdot CH_2\cdot C(CN)(CO_2Et)\cdot CH_2\cdot CN$.

This substance is formed in practically quantitative yield when 4·6 grams of sodium dissolved in 22·6 grams of alcohol are mixed with 22·6 grams of ethyl cyanoacetate, and then with 33·4 grams of iodoacetonitrile. The reaction is finished after heating on the water-bath for half an hour. The ester, which is extracted by ether in the usual manner, boils at 205°/18 mm.:

0·1970 gave 0·4089 CO_2 and 0·0813 H_2O. C=56·61; H=4·58.

$C_9H_9O_2N_3$ requires C=56·5; H=4·7 per cent.

$\alpha\beta\gamma$-*Tricyanopropane* (*Tricyanohydrin*),
$CN\cdot CH_2\cdot CH(CN)\cdot CH_2\cdot CN$.

Ten grams of ethyl $\alpha\beta\beta'$-tricyano*iso*butyrate are mixed with an equal volume of water, and the same volume of a 50 per cent. solution of potassium hydroxide. The oil dissolves when the mixture is shaken, and the solution is then at once rendered acid by acetic acid and raised to the boiling point. Carbon dioxide is eliminated, and an oil separates which solidifies on cooling. The compound is best recrystallised from ether, when it separates in long, colourless needles, melting at 47°:

0·1786 gave 0·3987 CO_2 and 0·0701 H_2O. C=60·88; H=4·36.

$C_6H_5N_3$ requires C=60·5; H=4·2 per cent.

The nitrile is soluble in hot water, and separates as an oil on cooling. It is sparingly soluble in cold ethyl alcohol or ether. When boiled with dilute sulphuric acid it is hydrolysed to tricarballylic acid.

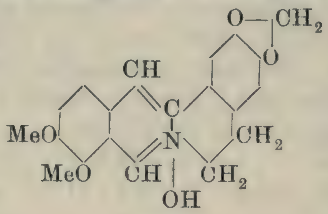
We were unable to detect the formation of any imino-compound from this nitrile by treatment with sodium ethoxide.

THE SORBY RESEARCH LABORATORY,
THE UNIVERSITY, SHEFFIELD.

CXC.—*iso*Quinoline Derivatives. Part VI. *neo*Oxyberberine.

By FRANK LEE PYMAN.

THE main features of the constitution of berberine were determined by Perkin (Trans., 1889, **55**, 63; 1890, **57**, 992) by a study of its oxidation products. Later, Gadamer (*Arch. Pharm.*, 1905, **243**, 42) and Perkin and Robinson (Trans., 1910, **97**, 321) proposed certain alterations in Perkin's original formula, and the constitution of this alkaloid is now recognised as that given below:

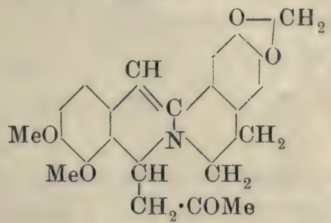


Berberine.

Perkin found that the careful oxidation of berberine, even in small quantities and with a limited amount of permanganate (in the presence of potassium carbonate), led to the formation of a mixture of a large number of products. This fact is readily explained by the above formula, by which the molecule is shown to contain two double linkings, at either or both of which oxidation would be expected to take place.

Now it seemed of interest to study the oxidation of a derivative of berberine in which one of these points of attack was protected, for in that case a more uniform oxidation product or a less complicated mixture of products should result. With this object in view the oxidation of berberineacetone was undertaken. This compound was first described by Gaze (*Zeit. Naturwiss, Halle*, 1890, **62**, 399)

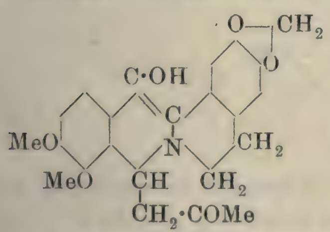
as a molecular compound before the nature of berberine was fully understood, but Gadamer (*loc. cit.*) recognised it later as a condensation product of the same type as anhydrocotarnineacetone, and suggested for it the formula (I), which satisfactorily explains its properties:



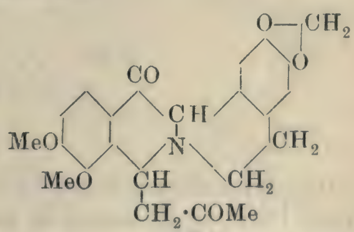
(I.)

Reference to the formula will show that this compound only contains one double linking. By hydrolysing it with dilute acids, however, the acetone can be removed and the second double linking replaced with the formation of berberine hydrochloride; this reaction is common to all similarly constituted *iso*quinoline derivatives, such as anhydrocotarnineacetone.

On oxidising berberineacetone, $C_{23}H_{23}O_5N$, in acetone solution with aqueous permanganate, a new colourless compound, $C_{23}H_{23}O_6N$, containing one more atom of oxygen, resulted. This substance, which was isolated in a yield of about 45 per cent. of the theoretical, has been designated neo*oxyberberineacetone.* Oxidation of berberineacetone would naturally be expected to take place at the double linking, and *neo*oxyberberineacetone would then have the formula (II) or the tautomeric form (III). The first of these, however, is eliminated by the insolubility of the compound in aqueous sodium hydroxide, but formula (III) satisfactorily accounts for its behaviour and that of its derivatives:



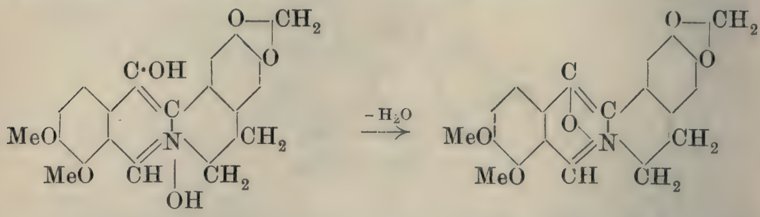
(II.)



(III.)

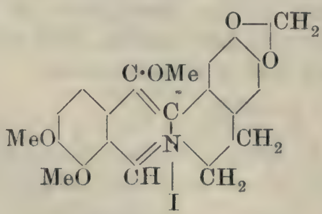
On hydrolysing *neo*oxyberberineacetone with dilute mineral acids, acetone is split off, and the salt of a quaternary base is produced, as is the case with all similarly constituted acetone-condensation products. The base obtained on treating this salt with alkali, however, is not the corresponding quaternary base, $C_{20}H_{19}O_6N$ (IV),

but a substance, $C_{20}H_{17}O_5N$, derived from it by the elimination of the elements of water. This compound is isomeric with oxyberberine and the *iso*oxyberberine recently described by Bland, Perkin, and Robinson (Proc., 1911, **27**, 59), and has been designated *neooxyberberine* (V). Its formation from the enolic form of the quaternary base may be represented as follows:



(IV.) (V.)

This formula depicts *neo*oxyberberine as a phenolbetaine, and this is justified by its behaviour, for it has the usual characteristics of such compounds (compare Decker and Dunant, *Annalen*, 1908, **358**, 296). Thus, it is golden-brown in colour, crystallises with a molecule of either alcohol or chloroform of crystallisation, and is liberated from its salts by means of sodium carbonate. Its salts with acids are of a much less intense colour than the base, and are derived from formula IV or the corresponding ketonic form by substitution. Definite proof of its phenolbetaine nature, however, is afforded by the fact that it yields with methyl iodide the iodide of a quaternary base containing three methoxyl groups, that is, one more than the parent compound. This substance, *methoxyberberinium iodide*, has the formula (VI) given below, and its

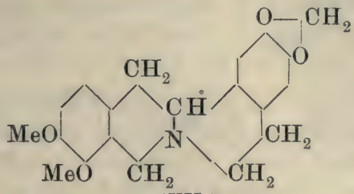


(VI.)

quaternary nature is shown by the fact that the corresponding base is not liberated by means of sodium carbonate, sodium hydroxide being requisite for this purpose.

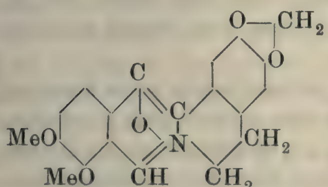
*neo*Oxyberberine also shows the behaviour, associated with phenolbetaines, of forming salts containing two molecules of the base to one of acid (compare Trans., 1910, **97**, 269); thus the hydrochloride has the formula HO·R⋮N·O·R⋮NCl, although the hydriodide has the normal constitution HO·R⋮N·I.

*neo*Oxyberberine readily furnishes tetrahydroberberine (VII) in good yield when reduced by means of tin and hydrochloric acid:



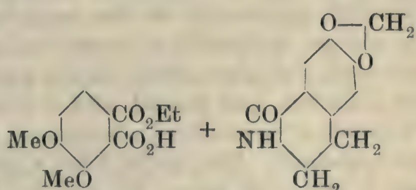
(VII.)

The most remarkable property of this compound, however, is the facility with which it undergoes spontaneous oxidation when exposed to the air in chloroform solution. So large a quantity as 25 grams of *neo*oxyberberine (containing 1EtOH) appeared to be completely decomposed after exposure to the air for eighteen days, and the reaction product gave 1-keto-6:7-methylenedioxytetrahydro*iso*quinoline (VIII) in a yield amounting to 53 per cent. of the theoretical, together with a quantity of one of the ethyl hydrogen hemipinates, probably the 1-ester (IX). Small quantities of other crystalline products, and a considerable amount of amorphous material, were produced at the same time. The formation of the two compounds isolated may be represented as follows:



(V.)

$+ EtOH + O_3 =$

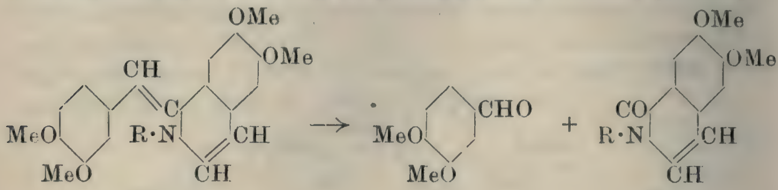


(IX.) (VIII.)

1-Keto-6:7-methylenedioxytetrahydro*iso*quinoline was, of course, one of the oxidation products of berberine isolated by Perkin (*loc. cit.*).

The degradation of *neo*oxyberberine in this manner recalls the analogous cleavage of the somewhat similarly constituted *N*-alkyl*iso*papaverines (X) into veratraldehyde (XI) and dimethoxy-

N-alkyl*iso*quinolones (XII), which Decker and Klauser (*Ber.*, 1904, **37**, 520) effected by drawing air through dilute alkaline solutions:



(X.) (XI.) (XII.)

Experimental.

The berberineacetone used in this investigation was prepared from commercial berberine sulphate by the method described by Gaze (*loc. cit.*). It melted and decomposed at 175° (corr.). (Found, C=70·0; H=5·9. Calc., C=70·2; H=5·9 per cent.)

Oxidation of Berberineacetone. Formation of neo*Oxyberberineacetone.*

The oxidation of berberineacetone, $C_{23}H_{23}O_5N$, to *neo*oxyberberineacetone, $C_{23}H_{23}O_6N$, involves the addition of one atom of oxygen. It has, however, been found advantageous to employ a quantity of permanganate corresponding with two atoms for the oxidation, and the following conditions have been found to give a satisfactory result.

Five and a-half grams of potassium permanganate were dissolved in 500 c.c. of water, and the solution was poured into a solution of 10 grams of berberineacetone in 500 c.c. of acetone at the laboratory temperature. The mixture was kept for fifteen minutes, then filtered from the separated manganese hydroxide, and the liquor somewhat evaporated on the water-bath. During the removal of the acetone, a quantity of crystals mixed with some resinous matter separated, and after nearly all the acetone had evaporated, the solid was collected, and ground with a little ethyl acetate, when 4·0 to 4·9 grams of neo*oxyberberineacetone*, melting at 228—229° (corr.), were obtained. This product has a more or less marked buff colour, but is otherwise pure. It may be decolorised by crystallisation from alcohol, using animal charcoal.

neo*Oxyberberineacetone*, $C_{23}H_{23}O_6N$ (III, p. 1691).

This base crystallises from absolute alcohol in colourless, transparent, hexagonal and trigonal plates, which melt and decompose at 228—229° (corr.), forming a dark red liquid. It is insoluble in water, and sparingly or very sparingly soluble in the usual organic

solvents, with the exception of warm chloroform, in which it is moderately easily soluble:

0·1527 gave 0·3773 CO_2 and 0·0786 H_2O. C = 67·4; H = 5·8.
0·1900 ,, 5·8 c.c. N_2 at 24° and 770 mm. N = 3·6.
$C_{23}H_{23}O_6N$ requires C = 67·5; H = 5·7; N = 3·4 per cent.

This base dissolves to some extent in cold dilute hydrochloric acid, but soon crystallises out as a very sparingly soluble, colourless *hydrochloride*. When warmed with dilute hydrochloric acid, the base yields a yellow solution, and eventually yellow, silky needles consisting of *neo*oxyberberine semihydrochloride. *neo*Oxyberberine-acetone is not attacked by hot aqueous sodium hydroxide, in which it is insoluble.

neo*Oxyberberine*, $C_{20}H_{17}O_5N$ (V, p. 1692).

Twelve grams of *neo*oxyberberineacetone were boiled for two hours under a reflux condenser with 1·2 litres of 1 per cent. aqueous hydrochloric acid. The almost insoluble powder gradually dissolved, forming a deep canary-yellow solution, from which a large quantity of curved, silky, yellow needles separated while the boiling was still in progress. The needles, which decomposed at 227° (corr.), consisted of *neo*oxyberberine semihydrochloride; they were not, however, collected, but converted into the base by adding 200 c.c. of 10 per cent. aqueous sodium hydroxide to the liquor and boiling it for another twenty minutes. The almost insoluble neo*oxyberberine* was then collected, and crystallised from alcohol, when 9·6 grams of the pure base (containing 1EtOH) were obtained; this yield amounts to 84 per cent. of the theoretical.

neo*Oxyberberine* crystallises from alcohol in long, golden-brown, prismatic needles, which contain one molecule of alcohol of crystallisation. It melts and decomposes at 275° (corr.), and is almost insoluble in boiling water, sparingly soluble in cold alcohol and most of the other usual organic solvents, but easily soluble in chloroform or hot alcohol:

0·1562 * lost 0·0176 at 100°. C_2H_6O = 11·3.
0·1528 * gave 0·3702 CO_2 and 0·0800 H_2O. C = 66·1; H = 5·9.
$C_{20}H_{17}O_5N,C_2H_6O$ requires C = 66·5; H = 5·8; C_2H_6O = 11·6 per cent.

0·1386 † gave 0·3469 CO_2 and 0·0615 H_2O. C = 68·3; H = 5·0.
0·1454 † ,, 5·0 c.c. N_2 at 20° and 773 mm. N = 4·1.
0·2102 † ,, , by Zeisel's method, 0·2758 AgI. MeO = 17·3.
$C_{20}H_{17}O_5N$ requires C = 68·3; H = 4·9; N = 4·0;
2MeO = 17·7 per cent.

* Air-dried. † Dried at 100°.

The molecular weight was determined by the ebullioscopic method in glacial acetic acid:

0·2344 † in 16·75 gave Δt 0·11°. M.W. = 322.
0·4988 † „ 16·75 „ Δt 0·20°. M.W. = 377.
$C_{20}H_{17}O_5N$ requires M.W. = 351.

*neo*Oxyberberine yields with acids sparingly soluble salts; it is insoluble in aqueous sodium hydroxide.

The *semihydrochloride* crystallises from water or alcohol in long, deep yellow, curved, silky needles, which decompose at 227° (corr.). It is very sparingly soluble in boiling water, and sparingly so in boiling alcohol. After crystallisation from water, and drying in the air, this salt has the composition $(C_{20}H_{17}O_5N)_2,HCl,3H_2O$:

0·1378 * gave 0·3058 CO_2 and 0·0676 H_2O. C = 60·5; H = 5·5.
0·1566 * „ 0·0294 AgCl. Cl = 4·6.
0·1266 * lost 0·0090 at 110°. H_2O = 7·1.
$(C_{20}H_{17}O_5N)_2,HCl,3H_2O$ requires C = 60·5; H = 5·2; Cl = 4·5; H_2O = 6·8 per cent.

The *hydriodide* crystallises from water in deep yellow needles, which decompose at 275° (corr.). It is very sparingly soluble in water, and crystallises with $1H_2O$:

0·2555 * lost 0·0099 at 100°. H_2O = 4·0.
$C_{20}H_{17}O_5N,HI,H_2O$ requires H_2O = 3·7 per cent.
0·2456 † gave 0·4532 CO_2 and 0·0834 H_2O. C = 50·3; H = 3·8.
0·3630 † „ 0·1780 AgI. I = 26·5.
$C_{20}H_{17}O_5N,HI$ requires C = 50·1; H = 3·8; I = 26·5 per cent.

Methoxyberberinium Salts (VI, p. 1692).

Methoxyberberinium iodide was prepared in almost theoretical yield by heating *neo*oxyberberine with methyl iodide in a sealed tube at 100° for two hours. It crystallises from boiling water, in which it is somewhat sparingly soluble, in golden-brown, prismatic plates, which melt to a black liquid at 256° (corr.), after sintering a few degrees earlier. It is anhydrous:

0·1651 gave 0·3086 CO_2 and 0·0634 H_2O. C = 51·0; H = 4·3.
0·1510 „ 0·0722 AgI. I = 25·8.
0·2158 „ , by Zeisel's method, 0·2989 AgI. MeO = 18·3.
$C_{21}H_{20}O_5NI$ requires C = 51·1; H = 4·1; I = 25·7; 3MeO = 18·9 per cent.

Methoxyberberinium chloride was prepared from the iodide by double decomposition with silver chloride. It is very readily soluble in water, and crystallises from this solvent in long, yellow needles, which contain 3 molecules of water of crystallisation, and

† Dried at 100°. * Air-dried.

melt at about 117° (corr.). It suffers decomposition when heated at 100°:

0·4000 * lost 0·0470 in a vacuum over H_2SO_4. $H_2O = 11·7$.

0·1982 * gave, by Zeisel's method, 0·2971 AgI. MeO = 19·8.

$C_{21}H_{20}O_5NCl,3H_2O$ requires $H_2O = 11·9$; 3MeO = 20·4 per cent.

After being dried in a vacuum over sulphuric acid:

0·1331 gave 0·3040 CO_2 and 0·0619 H_2O. C = 62·3; H = 5·2.

$C_{21}H_{20}O_5NCl$ requires C = 62·7; H = 5·0 per cent.

Aqueous solutions of this salt remain clear on the addition of sodium carbonate, but give with sodium hydroxide a yellow, amorphous precipitate, which is readily extracted by ether.

Reduction of neo*Oxyberberine. Formation of Tetrahydroberberine.*

Ten grams of *neo*oxyberberine were reduced by boiling with granulated tin and a large excess of hydrochloric acid in alcoholic solution until the originally yellow liquid had become nearly colourless. The liquor was then decanted from the tin, sufficiently evaporated to remove most of the alcohol, and diluted with about twice its volume of water, when a tin double salt separated, which was at first amorphous, but quickly became crystalline. This was collected, dissolved in about a litre of boiling water, treated with hydrogen sulphide, filtered from tin sulphide, and precipitated with aqueous sodium carbonate, when an oil separated which became partly crystalline on scratching. When this product was boiled with a little alcohol, 6·0 grams of tetrahydroberberine remained as a nearly colourless, chalky solid, which melted at 168—169° (corr.). The melting point of the base was unchanged by crystallising it from alcohol, and suffered no depression when the base was mixed with tetrahydroberberine prepared by the reduction of berberine. The identity of the base was further established by analysis (Found, C = 70·7; H = 6·3. Calc., C = 70·8; H = 6·2 per cent.), and also by the analysis of its hydrochloride, which crystallised from water in lozenge-shaped plates, melting and decomposing at 248—250° (corr.). (Found, C = 63·6; H = 6·0; Cl = 9·4. Calc., C = 63·9; H = 5·9; Cl = 9·4 per cent.)

Spontaneous Oxidation of neo*Oxyberberine.*

Twenty-five grams of *neo*oxyberberine (containing 1EtOH) were dissolved in 300 c.c. of chloroform, and kept for five weeks in a nearly full closed bottle in the dark. A considerable quantity of large, yellowish-brown plates gradually crystallised out, and proved to be *neo*oxyberberine containing a molecule of chloroform of crystal-

* Air-dried.

lisation. After being dried in the air overnight, the crystals were found to have slightly effluoresced, and on warming them, chloroform was readily given off:

0·2015 * lost 0·0487 at 100°. Loss = 24·2.

$C_{20}H_{17}O_5N,CHCl_3$ requires $CHCl_3$ = 25·4 per cent.

The crystals decomposed at 275° (corr.) when heated either alone or mixed with the base containing alcohol of crystallisation. The chloroform mother liquor left on evaporation a crystalline mass of *neo*oxyberberine in an almost pure condition (m. p. 260°). *neo*Oxyberberine is therefore not attacked by chloroform in the absence of air.

Twenty-five grams of *neo*oxyberberine (containing 1EtOH) were then dissolved in 300 c.c. of chloroform, and exposed to the air in a wide-mouthed glass bottle in a dark cupboard. After keeping for two days a drop of the solution readily gave a crystalline residue, but after five days only an amorphous residue was obtained in this way. The solution was exposed to the air for eighteen days in all, the chloroform lost on evaporation being replaced from time to time, and the original intense yellowish-brown colour gave place to a brown port-wine shade. The liquid was then filtered from a trace of yellow insoluble matter, extracted several times with dilute aqueous sodium carbonate to remove the acidic constituents, and the extract (*E*) set aside. The chloroform solution was then dried with anhydrous potassium carbonate, and evaporated nearly to dryness, when the residue became partly crystalline. It was mixed with a little benzene, filtered, and the residual pink, chalky, crystalline mass washed with benzene. From the filtrate only very small quantities of crystalline compounds were isolated, the chief constituent being a reddish-brown, amorphous substance. The air-dried, crystalline mass amounted to 8·3 grams, and melted at about 155°; on recrystallisation from benzene it gave first 4·8 grams of 1-keto-6 : 7-methylenedioxytetrahydro*iso*quinoline, melting at 185—186° (corr.). Perkin (*loc. cit.*) gives 181—182°. (Found, C = 62·4; H = 4·9. Calc., C = 62·8; H = 4·8 per cent.)

The benzene mother liquors gave on evaporation several small crops of crystals, melting at about 140°. On recrystallising these from water, however, a further 1·6 grams of 1-keto-6 : 7-methylenedioxytetrahydro*iso*quinoline separated, making in all 6·4 grams, that is, 53 per cent. of the theoretical; the aqueous mother liquors contained hemipinic acid.

The sodium carbonate extract (*E*) was acidified with hydrochloric acid, and completely extracted with ether. The ethereal extract was dried, and evaporated to low bulk, when 2·9 grams of 1-ethyl

* Air-dried.

hydrogen hemipinate separated in large, clear, colourless prisms, which melted at 148—149° (corr.), after drying at 100°. The ethereal filtrate on evaporation to dryness gave 3·1 grams of a slightly sticky, pink, crystalline mass, and on recrystallising this from water, using animal charcoal, a further 1·3 grams of 1-ethyl hydrogen hemipinate were obtained in long, colourless needles, which contained $1H_2O$, and melted at 148—149° (corr.), after drying at 100°. (Found, C = 56·5; H = 5·6. Calc., C = 56·7; H = 5·6 per cent.)

On saponifying this acid with 10 per cent. aqueous sodium hydroxide, acidifying, and extracting with ether, pure hemipinic acid was obtained. This melted and effervesced at 184—185° (corr.), solidified again on cooling, and then melted at about 165°. (Found, C = 52·9; H = 4·8. Calc., C = 53·1; H = 4·5 per cent.)

The ethyl hydrogen hemipinate thus obtained gave no coloration with ferric chloride in aqueous solution. It is therefore described as the 1-ester, since Wegscheider (*Monatsh.*, 1895, **16**, 38) states that the 1- and 2-ethyl hydrogen hemipinates are distinguished by the fact that the 2-ester gives with ferric chloride in aqueous solution a yellow coloration and turbidity, whilst the 1-ester does not. The ethyl hydrogen hemipinate from *neo*oxyberberine also agrees better in melting point with the 1-ester (m. p. 146·5—148·3°) than with the 2-ester (m. p. 144·5—145°). Wegscheider's 1-ester, however, contained no water of crystallisation, whilst the 2-ester crystallised from water in long needles containing $1H_2O$.

THE WELLCOME CHEMICAL WORKS.
DARTFORD, KENT.

CXCI. — *The Absorption Spectra of Various Chlorine and Bromine Derivatives of Benzene and Toluene as Vapours, in Solution and in Thin Films.*

By JOHN EDWARD PURVIS.

THE author has already given an account of the absorption spectra of monochloro- and monobromo-benzene as vapours, in solution, and in thin films (this vol., p. 811). The chief results proved that the vapours of these two substances exhibited a considerable number of bands which could be arranged in various groups; that equimolecular solutions in alcohol exhibited seven wide diffuse bands; and that very thin films exhibited seven wide diffuse bands which were also comparable with the solution bands.

The investigation has been continued with *o*- and *m*-dichloro- and

dibromo-benzene, and with *o*- and *m*-chloro- and bromo-toluene. The apparatus employed has been described in previous communications (*loc. cit.*).

Vapours.—o-Dichlorobenzene.

TABLE I.

The absorption bands in the vapour of *o*-dichlorobenzene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter.

Abbreviations: v.w. = very weak; w. = weak; m.w. = moderately weak; str. = strong; m.str. = moderately strong; narr. = narrow.

	19°. 763 mm. λ.	30°. 807 mm. λ.	45°. 833 mm. λ.	60°. 863 mm. λ.
	2780 v.w.	2780 v.w.		No bands.
	2779 v.w.	2779 v.w.		
	2776 m.w.	2777 v.w.		The rays were absorbed from about λ 2840, the Cd. lines 2748 and 2573 being visible.
	2774 m.w.	2775 w.		
	2773 m.w.	2773 w.		
A.	2770 w., narr.	2770 m.w.	2770 v.w.	
	2768 str.	2768 str.	2768 v.w.	
	2766 m.w.	2765 m.str.	2765 v.w.	
	2765 m.w.	2764 m.str.		
	2762 m.str.	2762 m.str.		
	2760 str.	2760 str.	2759 m.w.	
	2757 w., narr.	2757 w., narr.	2757 w., narr.	
	2754 w., narr.	2754 w., narr.	2754 w., narr.	75°.
	2751 w., narr.	2751 w., narr.	2752 w., narr.	893 mm.
B.	2745 v.w.	2746 v.w.	2750 w., narr.	λ.
	2740 v.w.	2741 v.w.		
	2738 v.w.	2738 v.w.	The rays were then absorbed from about λ 2740; the Cd. line 2573 was fairly strong and 2329, 2321, 2313 weak.	No bands.
	2737 v.w.	2737 v.w.		
	2706 v.w.			The rays were absorbed from about λ 2850.
	2702 m.str.	2703 v.w.		
	2695 m.str.	2696 v.w.		
C.	2690 m.w.	2690 v.w.		
	2688 m.str.	2689 v.w.		
	2686 w., narr.	2686 v.w.		
	2682 m.str.	2683 m.w.	8 bands.	
	2617 v.w.	2617 v.w.		
	2614 m.w.	2614 v.w.		90°.
	2606 w.	2606 v.w.		923 mm.
	2595 v.w.			λ.
	The rays wer then transmitted to Cd. 2265.	The rays were then feebly transmitted to λ 2420; the Cd. lines 2329, 2321 and 2313 were weak.		No bands.
	29 bands.	27 bands.		The rays were absorbed from about λ 2870, the Cd. line 2837 being just visible.

The absorption bands of the vapour were also photographed at a constant temperature of 15° and at the varying pressures of 736 mm., 606 mm., 456 mm., 306 mm., 156 mm., and 11 mm. The bands were similar to those described in table I at 19° and 763 mm., except that they were sharper, and, as the pressure decreased, only the stronger bands remained, so that at 11 mm. no bands were visible.

m-*Dichlorobenzene.*

TABLE II.

The absorption bands in the vapour of *m*-dichlorobenzene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. Abbreviations as before.

	19°. 763 mm. λ.	30°. 807 mm. λ.	45°. 833 mm. λ.	60°. 863 mm. λ.
A.	2788 v.w.	2788 v.w.	2788 v.w.	No bands.
	2783 v.w.	2784 v.w.	3783 v.w.	
	2780 m.w.	2780 m.w.	2780 m.str.	The rays were absorbed from λ 2820, the Cd. lines 2748 and 2573 being visible.
	2776 m.w.	2776 m.w.	2776 m.str.	
	2771 m.str.	2770 m.str.	2771 m.st	
	2768 str.	2768 str.	2768 m.str.	
	2764 v.w., narr.	2765 w., narr.	2765 v.w.	
	2762 str.	2762 str.	2762 str.	
B.	2759 v.w., narr.	2759 v.w., narr.	2759 v.w.	
	2756 v.w., narr.	2756 v.w., narr.	2756 v.w.	
			2754 v.w.	
	2752 v.w., narr.	2752 v.w., narr.	2752 v.w.	
	2745 v.w.	2745 v.w.	2746 w.	
	2740 v.w.	2741 m.w.	2740 m.str.	
	2739 m.w.	2738 m.w.	2739 v.w., narr.	
	2737 v.w.	2737 v.w.	2737 m.str.	
	2731 w.	2731 v.w.	2731 v.w.	75°.
C.	2708 v.w.	2709 m.w.	2709 w. and diff.	893 mm.
	2706 v.w.	2706 m.w.	2706 w. and diff.	λ.
	2700 m.str.	2700 m.w.	2700 w. and diff.	
	2694 str.	2694 m.str.	2694 v.w.	No bands.
	2690 m.str.	2690 m.str.	2690 v.w.	
	2685 str.	2685 str.	2685 m.w.	The rays were absorbed from λ 2840.
	2681 m.w.	2682 w.	2681 w.	
	2678 v.w.	2678 v.w.	2678 v.w.	
	2673 v.w.	2673 v.w.	2673 v.w.	
	2668 v.w.	2668 v.w.	2668 v.w.	
	2667 w.	2667 w.	2667 v.w.	
	2665 v.w.	2665 v.w., narr.		
	2660 v.w.	2660 v.w.	The rays were then absorbed from λ 2620, the Cd. lines 2573, 2329, 2321 and 2313 being visible.	
	2657 v.w.	2657 v.w.		
	2640 v.w.	2640 v.w.		
	2631 w.	2632 w.		
	2627 w.	2627 w.		
	2618 v.w.	2618 w.		90°.
	2616 v.w.	2615 v.w.		923 mm.
	2610 v.w.	2610 v.w.	28 bands.	λ.
	The rays were then transmitted to λ 2665.	The rays were then transmitted to λ 2265.		No bands.
	35 bands.	35 bands.		The rays were absorbed from λ 2870.

The absorption bands of the vapour were also photographed at a constant temperature of 15° and at varying pressures of 736 mm., 606 mm., 456 mm., 306 mm., 156 mm., and 11 mm. The bands were similar to those observed at 19° and 763 mm., except that they became sharper as the pressure decreased and only the stronger bands remained, so that at 11 mm. no bands were visible.

o-Dibromobenzene.

Table III.

The absorption bands in the vapour of *o*-dibromobenzene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. Abbreviations as before.

	18·5°. 763 mm. λ.	30°. 807 mm. λ.	45°. 833 mm. λ.	60°. 863 mm. λ.
A.	2778 v.w.	The bands at this temperature and pressure were similar to those observed at 18·5° and 763 mm., except that they were a little stronger. The rays were then absorbed from λ 2265.	2778 v.w.	2778 v.w.
	2777 v.w.		2777 v.w.	2776 v.w.
	2773 v.w.		2773 m.w.	2774 m.str.
	2772 v.w.		2772 m.w.	2772 w.
	2768 w.		2768 m.str.	2768 m.str.
	2765 v.w.		2765 w.	2765 v.w.
				2762 w.
	2759 v.w.		2759 m.w.	2759 m.str.
	2758 w.		2758 m.str.	2758 m.str.
	2757 w.		2757 str.	2756 str.
	2752 v.w.		2752 v.w., narr.	2753 w., narr.
	2750 w.		2750 m.str.	2750 str.
B.	2724 v.w.		2724 v.w.	
	2722 v.w.	30 bands.	2722 v.w.	
	2717 w.		2717 m.str.	2718 m.w.
	2710 v.w.		2710 m.w.	2710 m.w.
	2700 w.		2700 m.w.	2702 m.w.
	2695 w.		2695 str.	
	2690 v.w.		2690 v.w.	
	2689 v.w.		2689 m.w.	
	2686 w.		2686 str.	
C.	2678 v.w.		2678 v.w.	
	2667 v.w.		2667 v.w.	
	2666 w., narr.		2666 w., narr.	
	2662 w.		2662 m.str.	2663 w.
	2656 v.w.		2656 v.w.	
	2654 w.		2654 m.w.	The rays were then absorbed from λ 2640, the C . line 2573 being visible.
	2641 v.w.		2641 w.	
	2640 v.w.		2640 w.	
	2634 v.w.		2634 v.w.	
	2630 w.		2630 w.	
	The rays were then transmitted to λ 2265. 30 bands.		The rays were then absorbed from λ 2430; the Cd. lines 2321 and 2313 were just visible. 30 bands.	75°. 893 mm. λ. No bands The rays were absorbed from λ 2810, the Cd. lines 2748 and 2573 being visible. 90°. 923 mm. λ. No bands. The rays were absorbed from λ 2850.

Experiments with the vapour at a constant temperature and varying pressures were not conducted.

m-*Dibromobenzene.*

Table IV.

The absorption bands in the vapour of *m*-dibromobenzene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. Abbreviations as before.

	18° 757 mm. λ.	30°. 801 mm. λ.	45° 822 mm. λ.	60 . 857 mm. λ.
A.	2785 v.w.	The bands at this temperature and pressure were similar to those observed at 18° and 757 mm., except that they were a little stronger.	2785 v.w.	2786 v.w.
	2782 v.w.		2782 v.w.	2781 v.w.
	2780 v.w.		2780 v.w.	2779 v.w.
	2778 w.		2778 m.str.	2777 m.str.
	2774 v.w.		2774 w., narr.	2774 w., narr.
	2772 w.		2772 str.	2773 str.
B.	2713 v.w.		2713 v.w.	2713 v.w.
	2710 v.w.		2710 v.w.	2710 v.w.
	2706 w.		2706 m.str.	2707 m.str.
	2705 w.		2705 w., narr.	
	2701 w.	The rays were then transmitted to λ 2265, but they were weaker than at 18° and 757 mm.	2701 m.w.	2701 m.str.
C.	2638 v.w.		2638 v.w.	2638 v.w.
	2633 w.		2633 m.w.	2632 v.w.
	The rays were then transmitted to λ 2265.		The rays were then transmitted to λ 2370, the Cd. lines 2329, 2321, and 2313 being visible	The rays were then transmitted to λ 2420.
	13 bands.	13 bands.	13 bands.	12 bands.
				75°. 887 mm. λ.
				No bands.
				The rays were absorbed from about λ 2770, the Cd. lines 2748 and 2573 being fairly strong.
				90°. 917 mm. λ.
				No bands.
				The rays were absorbed from about λ 2840; the Cd. lines 2748 and 2573 were just visible.

Experiments with the vapour at a constant temperature and varying pressures were not conducted.

o-Chlorotoluene.

TABLE V.

The absorption bands in the vapour of *o*-chlorotoluene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. Abbreviations as before.

	18°. 756 mm. λ.	30°. 800 mm. λ.	45°. 826 mm. λ.	60°. 856 mm. λ.
A.	2755 v.w.	The bands at this temperature and pressure were similar to those at 18° and 756 mm. and the rays were absorbed from λ 2265.	2755 w.	No bands.
	2728 v.w.		The rays were then absorbed from λ 2748, the strong Cd. lines 2573 to 2265 being visible.	The rays were absorbed from λ 2770, the Cd. lines 2329, 2321 and 2313 being visible.
	2725 v.w.			
	2724 m.w.			
	2720 m.w			
	2719 m.str.			
	2716 v.w., narr.			
	2714 str.			
B.	2706 v.w.			
	2704 v.w.	23 bands.	1 band.	
	2696 v.w.			
	2690 v.w.			75°. 886 mm. λ.
	2686 m.w.			
	2680 m.w.			No bands.
	2673 v.w.			The rays were absorbed from λ 2840, the Cd. lines 2329, 2321 and 2313 being just visible.
	2672 v.w.			
	2668 v.w.			
	2660 v w.			
	2651 v.w.			
	2646 w.			
	2640 w.			
	2634 m.w.			
	2632 m.w.			
	The rays were then transmitted to λ 2265.			90°. 916 mm. λ.
	23 bands.			No bands.
				The rays were absorbed from λ 2850.

m-*Chlorotoluene*.—Table VI.

The absorption bands in the vapour of *m*-chlorotoluene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. Abbreviations as before.

	19°. 756 mm. λ.	30°. 800 mm. λ.	45°. 826 mm. λ.	60°. 856 mm. λ.
I.	2740 v.w.	The bands at this temperature and pressure were similar to those observed at 19° and 756 mm., and the rays were absorbed from λ 2265, but the Cd. lines were weaker than at 19°.	No bands.	No bands.
	2737 m.w.			
	2736 m.w.	20 bands.	The rays were absorbed from λ 2748, but the Cd. lines 2573, 2329, 2321, 2313 and 2288 were visible.	The rays were absorbed from λ 2780; the Cd. lines 2329, 2321 and 2313 were just visible.
	2734 m.w.			
	2732 m.w.			
II^A.	2717 v.w.			
	2711 v.w.			
	2706 m.w.			
	2701 m.w.			
	2671 v.w.			
III^A.	2667 v.w.			
	2666 m.w.			
	2664 m.w.			
	2661 v.w.			
IV^A.	2648 w.			
	2640 v.w.			
	2635 w.			
	2634 w.			
	2598 w.			
	2592 w.			

The rays were then transmitted to λ 2265.

20 bands.

75°. 886 mm. λ.	90°. 916 mm. λ.
No bands.	No bands.
The rays were absorbed from λ 2810.	The rays were absorbed from λ 2830.

o-*Bromotoluene*.—Table VII.

The absorption bands in the vapour of *o*-bromotoluene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. Abbreviations as before.

	19°. 757 mm. λ	30°. 801 mm. λ.	45°. 827 mm. λ.	60° 857 mm. λ.
A.	2761 v.w.	The bands at this temperature and pressure were similar to those observed at 19° and 757 mm.	2761 v.w.	No bands.
	2759 v.w.		2759 v.w.	
	2756 v.w.	15 bands.	2757 v.w.	The rays were absorbed from λ 2780; the Cd. lines 2748 and 2573 were just visible.
	2753 v.w.		2753 v.w.	
	2748 v.w.		2748 m.str.	
B.	2737 v.w.		The rays were then absorbed from 2740; the Cd. line 2573 was visible.	
	2731 v.w.			
	2728 v.w.		5 bands.	
	2727 v.w.			
	2720 m.str.			
	2715 m.str.			
	2689 v.w.			
	2683 v.w.			
	2676 v.w.			
	2671 m.w.			

The rays were then transmitted to Cd. 2313.

15 bands.

75°. 887 mm. λ.	90°. 917 mm. λ.
No bands.	No bands.
The rays were absorbed from λ 2820.	The rays were absorbed from λ 2860.

m-*Bromotoluene.*

TABLE VIII.

The absorption bands in the vapour of *m*-bromotoluene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. Abbreviations as before.

<table>
<tr><th colspan="2">19°.
757 mm.
λ.</th><th>30°.
801 mm.
λ.</th><th>45°.
827 mm.
λ.</th><th>60°.
857 mm.
λ.</th></tr>
<tr><td>I^A.</td><td>2759 v.w.
2756 v.w.</td><td rowspan="6">The bands at this temperature and pressure were similar to those observed at 19° and 757 mm. The rays were then transmitted to λ 2288.

19 bands.</td><td rowspan="6">The bands at this temperature and pressure were similar to those at 30°. The rays were then transmitted to λ 2380.

19 bands.</td><td rowspan="6">No bands.

The rays were absorbed from λ2750, but the Cd. line 2573 was visible.

75°.
887 mm.
λ.
No bands.

The rays were absorbed from λ 2780, but the Cd. lines 2748 and 2573 were just visible.

90 .
917 mm.
λ.
No bands.

The rays were absorbed from λ 2820.</td></tr>
<tr><td>II^A.</td><td>2745 v.w.
2740 v.w.
2738 m.w.
2736 w.
2733 m.w.
2731 w.</td></tr>
<tr><td>III^A.</td><td>2717 v.w.
2714 v.w.
2711 v.w.
2709 v.w.
2706 v.w.</td></tr>
<tr><td>IV^A.</td><td>2673 m.w.
2670 m.w.
2667 m.w.
2664 m.w.
2662 m.w.</td></tr>
<tr><td></td><td>2650 v.w.</td></tr>
<tr><td colspan="2">The rays were then transmitted to 2313.

19 bands.</td></tr>
</table>

At the increased temperatures and pressures the bands in all the vapours became a little more diffuse; and, at the highest temperatures and pressures, the bands disappeared consequent on the overlapping general absorption. These phenomena are exactly similar to those observed in the vapours of other substances, an account of which has been given in previous communications. The groups of bands, and the number of bands, are fewer than were found in the vapours of chloro- and bromo-benzene (*loc. cit.*); and they are also fewer than those in the vapours of benzene and toluene as described by Hartley (*Phil. Trans.*, 1908, *A*, **208**, 475). The maximum number of bands in benzene and toluene vapours were 84 and 22 respectively, and the maximum number in the vapours of chloro- and bromo-benzene were 73 and 62 respectively.

Further, Hartley divided the vapour bands of benzene into nine

groups, and those of toluene into six groups; and the author divided the bands in the vapours of chloro- and bromo-benzene into five principal groups. On comparing the bands of the vapours of *o*- and *m*-dichlorobenzene, the larger number of bands may be divided into three principal groups, but the most refrangible bands were so weak that no grouping could be attempted. These three primary groups, however, are not similar to each other, although the bands of group A are fairly comparable in both substances, and they are also comparable with the groups of bands I and II in the vapours of chloro- and bromo-benzene. Further, there is a group of bands A in *o*- and *m*-dibromobenzene which are fairly comparable with each other, and also with the group of bands A in the vapours of the corresponding dichlorobenzene compounds, and also with the bands I and II in the vapours of chloro- and bromo-benzene. The groups of bands B and C are quite different; the individual bands are wider and more diffuse, and weaker in all the disubstituted compounds. With regard to *o*-chloro- and *o*-bromo-toluene, the two groups of bands A and B are fairly comparable, and the group A is comparable with the group A of *o*- and *m*-dichloro- and dibromo-benzene. On the other hand, the four small groups into which the bands of *m*-chloro and *m*-bromo-toluene are divided are comparable in appearance with each other, but they are not comparable with any of the groups of *o*-chloro- and *o*-bromo-toluene. These four groups of the meta-compounds are a series of weak, rather closely packed bands.

At the same time it should be observed that no very close comparison of some of these bands is possible, because of the images of various bright, strong lines of cadmium which was used as the source of light. This drawback is particularly marked by the presence of the strong cadmium line 2748; and, to a less degree, by the cadmium lines 2764 and 2775. Their images overshadow the weaker bands as well as obliterate bands which are in the same neighbourhood.

General Results of the Vapours.

The general results of the preceding observations are that (1) each vapour possesses a considerable number of absorption bands which can be divided into groups; (2) these groups are comparable in appearance in the vapours of *o*- and *m*-dichloro- and dibromo-benzene, where there are three primary groups; and with *o*-chloro- and *o*-bromo-toluene in which there are two primary groups; (3) the groups in *m*-chloro- and *m*-bromo-toluene are comparable with each other, but they are not comparable with the groups of bands of the other substances. The experiments were repeated several

times with two freshly prepared samples of each substance, which were redistilled several times, so that there can be no doubt about the accuracy of the differences observed in the toluene compounds; (4) the effect of introducing an atom, like chlorine or bromine, or a group of atoms like a methyl group, is to diminish the number of vapour bands; and the diminution is more marked in the case of a methyl group, although it is lighter than the halogens; (5) with increased temperature and pressures the separate bands become more diffuse.

Solutions in Alcohol.

Pauer (*Wied. Ann.*, 1897, **61**, 363) found three bands in alcoholic solutions of toluene; and Baly and Collie (Trans., 1905, **87**, 1332) found the same number. The latter authors (*loc. cit.*) and Baly and Ewbank (*ibid.*, 1355) describe the absorption spectra of chlorobenzene and the three dichlorobenzenes and chlorotoluenes. Later Baly (this vol., p. 856) repeated the observations, and found that these substances had more absorption bands than had been previously described. The author (*loc. cit.*) has confirmed the observations, and also found that bromobenzene exhibited seven bands. These bands are comparable with each other, except that they differ in position dependent on the weights of the molecules. Further, equimolecular solutions of the substances of the present investigation have been studied; and the observed bands are completely different from those of the vapours. The solution bands are wide and diffuse, and slightly more diffuse on the less refrangible edges, and they are fewer in number than the vapour bands. It is not easy to measure the edges of the diffuse solution bands; the positions of maximum absorption are much easier to measure, and they are called the heads of the bands. The following numbers are the positions of the heads of the bands in $M/100$-solutions photographed through thicknesses of 4 mm.

$M/100$-o-*Dichlorobenzene.* λ.	$M/100$-m-*Dichlorobenzene.* λ.
2770 f.str., wide	2776 f.str., wide
2696 f.str., wide	2700 f.str., wide
2615 w., wide	2621 w., wide
2574 v.w., wide	2560 v.w., wide

$M/100$-o-*Dibromobenzene.* λ.	$M/100$-m-*Dibromobenzene.* λ.
2779 f.str., wide	2780 f.str., wide
2710 f.str., wide	2720 f.str., wide
2630 w., wide	2645 w., wide
? 2580 v.w.	? 2590 v.w.

M-100-o-*Chlorotoluene*.	*M*/100-m-*Chlorotoluene*.
λ.	λ.
2730 f.str., wide	2747 f.str., wide
2660 v.w., wide	2675 w., wide
? 2580 v.w., wide	? 2596 v.w., wide

M/100-o-*Bromotoluene*.	*M*/100-m-*Bromotoluene*.
λ.	λ.
2745 f.str., wide	2750 f.str., wide
2670 w., wide	2680 f.str., wide
? 2595 v.w.	? 2610 v.w.

The bands marked ? are very weak, and not easily distinguished. The wide diffuse solution bands of each substance are fairly comparable with the corresponding ones in the other substances: they differ only in position dependent on the weight of the substituting atoms or groups of atoms. The number of bands of the dihalogen derivatives is fewer than in the monohalogen compounds, as described before (*loc. cit.*), and there are fewer bands in the toluene compounds than in the dihalogen compounds.

Liquids in Thin Films.

In previous communications (Trans., 1910, **97**, 692, 1035, 1649, 1546, and this vol., p. 811) the author has given accounts of investigations of very thin films of various substances varying between thicknesses of 0·01 and 0·001 mm. Through these films general absorption only was observed. Thinner films were obtained by gently pressing a drop of the liquid between two quartz plates, and selective absorption was then noticeable. The following numbers give the heads of these liquid bands at the places of maximum absorption.

o-*Dichlorobenzene*.	m-*Dichlorobenzene*.
λ.	λ.
2787 f.str., wide	2790 f.str., wide
2702 f.str., wide	2703 f.str., wide
2630 v.w., wide	2635 v.w., wide
? 2578 vw., wide	? 2583 v.w., wide

o-*Dibromobenzene*.	m-*Dibromobenzene*.
λ.	λ.
2810 f.str., wide	2815 f.str., wide
2720 f.str., wide	2730 f.str., wide
2650 w., wide	2655 w., wide
? 2580 v.w., wide	? 2585 v.w., wide

o-*Chlorotoluene*.	m-*Chlorotoluene*.
λ.	λ.
2751 f.str., wide	2755 f.str., wide
2676 f.str., wide	2680 f.str., wide
? 2605 v.w., wide	?? 2610 v.w., wide

o-*Bromotoluene.* λ.	m-*Bromotoluene.* λ.
2760 f.str., wide	2765 f.str., wide
2685 w., wide	2690 f.str., wide
? 2615 v.w.	?? 2620 v.w.

Pauer (*loc. cit.*) examined thin films of toluene, and found three bands. The author has also examined thin films of toluene pressed between quartz plates, and found three bands, the heads of which are:

Toluene. λ.
2690 str., wide
2625 str., wide
2560 v.w., wide

All these liquid bands are wide and diffuse, and they are more diffuse on the less than on the more refrangible edges. Their general appearance is comparable with the corresponding solution bands. The bands marked ? are very weak, and not clearly distinguished.

Discussion of Results.

In discussing these results, the phenomena to be explained are of several kinds. First, there is the considerable number of vapour bands; secondly, the smaller number of solution bands, and of a different type; and thirdly, the smaller number of bands of the thin films which are closely comparable in appearance with the solution bands. Some explanation is also necessary to account for the diminution in the number of bands, whether in the vapours or in the thin films or in the solutions which accompanies the substitution of one or two hydrogen atoms of the benzene nucleus by a halogen atom or a methyl group.

To consider the vapours first, it may be that the vibrations of the atoms of the benzene molecule are unimpeded by any exterior forces except those which are the result of the encounters of the molecules themselves. The internal vibrations of the atoms which produce selective absorption are not subjected to any external disturbing force except those which are given to them by variations in the temperature and pressure. The general effect of these forces is apparent, not in any striking alteration in the type of each band, but in a greater diffuseness and widening. When one or more of the hydrogen atoms are replaced by a methyl group or a halogen atom, the number of vibrations in a given time is restricted with a consequent diminution in the number of the more refrangible bands. But the type of the less refrangible group is similar to the less refrangible group of bands of the original benzene molecule, and differs only in position, controlled generally by the

weight of the introduced radicle. This is true for chloro- and bromo-benzene, for *o*- and *m*-dichloro- and dibromo-benzene, and for *o*-chloro- and -bromo-toluene; but for *m*-chloro- and -bromo-toluene no such similarity exists. In these substances the orientation, the type of the inserted radicle, and the number and type of its constituent atoms, influence the nature of the selective absorption; and, in this connexion, the radiant energy of the source of light may be of paramount importance. A definite amount of energy may be absorbed, and each atom will absorb an amount dependent on its intrinsic characters and its differential relation with the other atoms of the nucleus and of the side-chains; so that space relations, as well as the number and type of the side-chains, will determine the direction of the vibrations, not only of each oriented atom or group of atoms, but also of all the atoms of the molecule, and the final adjustment will depend on the correlated oscillations or vibrations of a complex series of disturbances. In some such direction, the differences in the bands of *m*-chloro- and -bromo-toluene from those of the ortho-compounds may be explained.

When the molecules are dissolved in alcohol, their movements are considerably altered. The separate constituents of the groups of vapour bands are no longer apparent. The numerous bands have been reduced to a few large diffuse ones; and, as in the vapours, the displacement of the hydrogen atoms by methyl groups or by halogen atoms is to restrict the number of bands, and to eliminate the more refrangible bands. The author has suggested before (*loc. cit.*) that the solvent not only restrains the vibrations or oscillations of the benzene ring and its constituent atoms or side-chains by virtue of the tensional forces at the surfaces of the two types of molecules, namely, the dissolved substance and the solvent, but that it also acts as a barrier to the number of encounters, as well as an absorbent of a part of the radiant energy. The external influence of the solvent is more powerful than when the molecules are in the vaporous condition, and the total result is to modify the internal vibrations to such an extent as to alter the type of selective absorption. The number of individual bands is greatly decreased, although the characteristic broad diffuse solution bands are generally comparable with groups of the vapour bands; but they differ in position as a result of the damping force of the solvent.

In the liquids the selective absorption is only apparent in the thinnest films. The author has shown before that when the thin films were between 0·01 mm. and 0·001 mm. thick, no selective absorption was obtainable. In the later experiments, selective absorption was only obtained by pressing closely the quartz plates

binding the films. Such excessively thin films can no longer be called liquids. Their physical condition is more like that of a vapour under very high pressure; the closely packed molecules of the films must exert a tensional effect upon each other; the restraining influences on the vibrations must be very great; and the selective absorption approximates towards the conditions implied by a solution or by a vapour under very high pressure. The result is exhibited in the appearance of wide diffuse bands not unlike those of the solutions; and the greater shift of the bands towards the red end is caused by the closely packed molecules interfering with the rate of vibration.

The author is engaged in a comparative study of the corresponding iodine compounds and of other compounds of benzene and toluene; and he has again to thank the Government Grant Committee of the Royal Society, by whose assistance the greater part of the cost of the apparatus used in the investigation was defrayed.

University Chemical Laboratory,
Cambridge.

CXCII.—*Substances Related to Cochenillic and Carminic Acids. Part I. Synthesis of the Methyl Ether of β- and of γ-Coccinic Acid.*

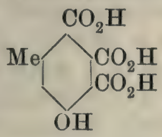
By Andrew Norman Meldrum (late Carnegie Research Fellow).

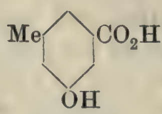
The discovery of cochenillic acid and the establishment of its constitution form an important addition to our knowledge of the colouring matter contained in cochineal. Liebermann and Voswinckel discovered the acid amongst the oxidation products of cochineal-extract and of carminic acid (*Ber.*, 1897, **30**, 688), and by a study of its degradation products they proved it to have the constitution represented in formula I (*Ber.*, 1897, **30**, 1733).

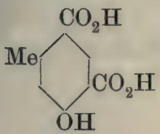
Constitution of the Degradation Products of Cochenillic Acid.

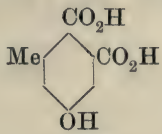
Liebermann and Voswinckel found that cochenillic acid, when heated under various conditions, yields three other acids, two of which are identical with substances already known. One of them proved to be 5-hydroxy-*m*-toluic acid (II), whilst another, *α*-coccinic acid, as they named it, is identical with *m*-hydroxyuvitic acid (III *α*). The third degradation product was a new substance, and was called

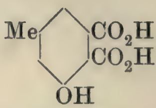
β-coccinic acid. It has the constitution shown in formula III β, although, as a hydroxyphthalic acid derived from cochenillic acid,


(I.)


(II.)


(III α.)


(III β.)

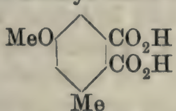

(III γ.)

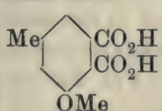
it might equally well have the formula III γ. It does not, however, give a distinct colour-reaction with ferric chloride, as a substance of that type ought to do. The constitution of the β-acid being thus a settled matter, the name γ-coccinic acid can be assigned to the substance (hitherto unknown) of formula III γ.

Synthesis of Substances Related to Cochenillic Acid.

5-Hydroxy-*m*-toluic acid has been obtained from *m*-toluic acid by Jacobsen (*Ber.*, 1881, **14**, 2357), and from ethyl acetoneoxalate by Claisen and Miller (*Ber.*, 1889, **22**, 3272).* *m*-Hydroxyuvitic acid has been synthesised by Oppenheim and Pfaff (*Ber.*, 1874, **7**, 929; 1875, **8**, 884), Oppenheim and Precht (*Ber.*, 1876, **9**, 321), Claisen (*Annalen*, 1897, **297**, 43), and Errera (*Ber.*, 1899, **32**, 2785). These syntheses were carried out without any explicit intention of obtaining substances related to carminic or cochenillic acid. In the present paper the author gives an account of an attempt to synthesise β-coccinic acid. The starting point of the work is the substance 5-hydroxy-*m*-toluic acid, which, it may be emphasised here, can be obtained, on the one hand, by the degradation of carminic acid, and, on the other, by synthesis from acetone and ethyl oxalate.

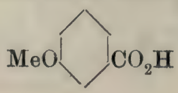
The work actually accomplished has resulted in the synthesis of two isomeric substances, one of which is the methyl ether (IV β) of the intended acid, whilst the other, from the nature of the synthetic method employed, can have only the constitution IV γ, that is, it is the methyl ether of γ-coccinic acid.


(IV β.)

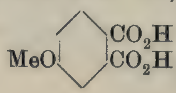

(IV γ.)

* The second synthesis was elucidated by J. Bishop Tingle (*Diss.*, München, 1889).

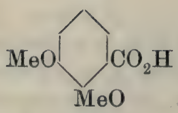
These two substances, IV β and IV γ, are methoxyphthalic acids, and a method of synthesising such acids is due to Fritsch. The net result of the method is to introduce a second carboxyl group in the ortho-position with respect to a carboxyl group already in the molecule, and in the para-position to a methoxy-group. Thus *m*-methoxybenzoic acid (V) leads to 4-methoxyphthalic acid (VI), whilst 2:3-dimethoxybenzoic acid (VII) furnishes hemipinic acid (VIII) (*Annalen*, 1897, **296**, 358; 1898, **301**, 360):



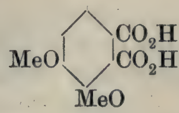
(V.)



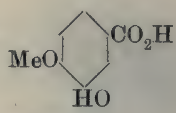
(VI.)



(VII.)

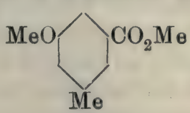


(VIII.)

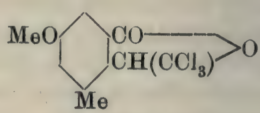


(IX.)

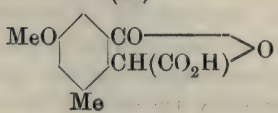
The series of reactions involved in Fritsch's synthesis is well exemplified in the case of β-coccinic acid. 5-Hydroxy-*m*-toluic acid is converted into the methyl methoxy-ester (X), and this, in the presence of sulphuric acid, condenses with chloral, with production of 5-methoxy-3-methyl-2-trichloromethylphthalide (XI β). The latter, on hydrolysis, gives 5-methoxy-3-methylphthalide-2-carboxylic acid (XII β), which, when heated, loses carbon dioxide, forming 5-methoxy-3-methylphthalide (XIII β). This phthalide, on oxidation, yields 5-methoxy-3-methylphthalic acid (IV β), that is, the methyl ether of β-coccinic acid:



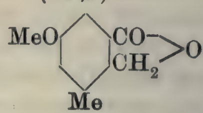
(X.)



(XI β.)



(XII β.)



(XIII β.)

So far, the synthesis proved a success. It was found impracticable, however, to obtain β-coccinic acid by hydrolysis of the methyl ether. Treatment in the usual way with hydriodic acid resulted in a large yield of 5-hydroxy-*m*-toluic acid. Presumably β-coccinic acid was formed, and was decomposed by the hydriodic acid. This is in accordance with the known behaviour of certain hydroxyphthalic acids on treatment with hydriodic or hydrochloric acid: the tendency is to the formation of a *m*-hydroxybenzoic acid. 3-Hydroxyphthalic

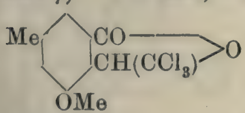
acid (Rée, *Annalen*, 1886, **233**, 234) and 2-hydroxyterephthalic acid (Burkhardt, *Ber.*, 1877, **10**, 145) give *m*-hydroxybenzoic acid in each case, whilst hemipinic acid (VIII) gives *iso*vanillic acid (IX) (Wegscheider, *Sitzungsber. K. Akad. Wiss. Wien*, 1882, **85**, 963, 968).

For purposes of identification, therefore, the methyl ether of β-coccinic acid was prepared from cochenillic acid. This specimen, of natural origin, was found by the "mixed melting-point" method to be as nearly as possible the same as the synthetic substance, and the corresponding anhydrides proved unquestionably the same.

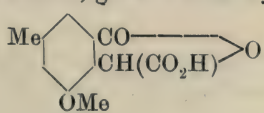
γ-*Coccinic Acid.*

A complication arose in the course of the synthesis just described: hydrolysis of the trichloromethylphthalide produced, not one, but two carboxylic acids. The two acids are not only isomeric with one another, but very similar in chemical behaviour: each, when heated, gives a phthalide, and each phthalide, on oxidation, gives a phthalic acid. The explanation of this, which seems the most likely one, is, that the trichloromethylphthalide is really a mixture of two isomeric substances, namely, 5-methoxy-3-methyl-2-trichloromethylphthalide (XI β) and 3-methoxy-5-methyl-2-trichloromethylphthalide (XI γ). The assumption here is that chloral condenses with the methyl methoxytoluate in the ortho- as well as in the para-position with respect to the methoxy-group, and that there results a mixture of two trichloromethylphthalides, which, being isomorphous with one another, cannot be separated by crystallisation. There is nothing intrinsically impossible in the supposition that condensation can occur in both positions, although Fritsch observed no instance of it in his work.

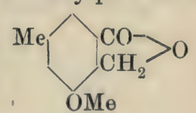
Hydrolysis of 3-methoxy-5-methyl-2-trichloromethylphthalide (XI γ) must give 3-methoxy-5-methylphthalide-2-carboxylic acid (XII γ). The acid, when heated, gives 3-methoxy-5-methylphthalide



(XI γ.)



(XII γ.)

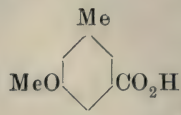


(XIII γ.)

(XIII γ), and the latter on oxidation yields 3-methoxy-5-methylphthalic acid (IV γ), the methyl ether of γ-coccinic acid.

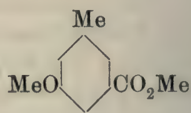
As a basis for further work, γ-coccinic acid is of unusual importance. By subjecting it, for instance, to chemical changes similar to those employed for obtaining β-coccinic acid, of course with suitable modifications, one might expect to obtain synthetic cochenillic acid.

Experimental.

5-*Methoxy*-m-*toluic Acid*,  .

The 5-hydroxy-*m*-toluic acid required for this investigation was synthesised from acetone and ethyl oxalate much according to details given by Tingle (*loc. cit.*) and by Meldrum and Perkin (Trans., 1909, **95**, 1896). The hydroxy-acid was converted into the methoxy-acid by methyl sulphate in the usual way. A small amount of the product was recrystallised from glacial acetic acid; it separated in needles, and melted at 134°. Titration with standard alkali showed that it was the expected substance.

0·0973 neutralised 5·89 c.c. 0·1*N*-sodium hydroxide solution, or 0·02356 NaOH, whilst this amount of the acid $C_9H_{10}O_3$ should neutralise 0·02345.

Methyl 5-*Methoxy*-m-*toluate*,  .

The methoxy-acid (56 grams) was dissolved in methyl alcohol (180 c.c.), and, after the addition of sulphuric acid (8 c.c.), the solution was boiled under a reflux condenser during four hours. The product was cooled, dissolved in ether, and washed with water so as to remove all sulphuric acid and methyl alcohol. The ethereal solution was dried, and distilled. The ester boiled at 262—268°/752 mm. Yield, 52 grams. As a check, the crude ester was analysed:

0·1446 gave 0·3521 CO_2 and 0·0830 H_2O. C = 66·4; H = 6·4.

$C_{10}H_{12}O_3$ requires C = 66·7; H = 6·7 per cent.

5-*Methoxy*-3-*methyl*-2-*trichloromethylphthalide* (XI β) and 3-*Methoxy*-5-*methyl*-2-*trichloromethylphthalide* (XI γ).

Methyl 5-methoxy-*m*-toluate (10 grams), chloral hydrate (10 grams), and sulphuric acid (50 c.c.) were mixed together, when heat was evolved, and the materials formed a clear solution. After twenty-four hours the solution was diluted with water, when a heavy liquid separated and soon became solid. The solid was collected, washed with 50 per cent. alcohol, and dried. The yield was 15 grams.

The substance was crystallised from methyl alcohol. When pure it is white, and melts at 116—117°. The crystals have the shape of

oblique double pyramids, passing into rectangular plates with the corners truncated:

0·2037 gave 0·2968 AgCl. Cl = 36·0.

$C_{11}H_9O_3Cl_3$ requires Cl = 36·0 per cent.

The product of the above condensation, having been found on hydrolysis to give rise to two isomeric acids, may possibly itself consist of a mixture of two isomeric trichloromethylphthalides. The material was therefore crystallised repeatedly from various solvents, namely, acetone, acetic acid, methyl alcohol, and ether, and in this way a solid which melted at 117° was obtained. This on hydrolysis was found to yield two acids as before. It is therefore impracticable to separate the two isomeric trichloromethylphthalides, of which it probably consists, by crystallisation.

Hydrolysis of the Trichloromethylphthalides. Preparation of 5-Methoxy-3-methylphthalide-2-carboxylic Acid (XII β).

Numerous experiments were made in order to ascertain the best way of hydrolysing the trichloromethylphthalides, and in the end the following process was adopted. The phthalide (15 grams) in a state of fine powder was added to about its own weight of alcohol, the mixture was heated until the alcohol began to boil, and then the hot pasty mass was added to a solution of sodium hydroxide (15 grams) in water (75 c.c.). Heat was evolved, and the alkaline solution was cooled so as to keep the temperature at 50—60°. The phthalide dissolved almost completely, and the solution became dark in colour.

Minute crystals were formed in the solution, of a substance which proved to be a sodium salt. It was collected, dissolved in water, and purified by boiling with animal charcoal. The free acid, obtained by acidifying the solution of this sodium salt, is a white substance, which, when pure, melts at 170°. From acetone it crystallises in prisms and plates with oblique ends. For analysis it was crystallised from acetic acid, and finally from water.

0·2575 neutralised 11·68 c.c. 0·1*N*-sodium hydroxide solution, or 0·0467 NaOH, whilst this amount of the acid $C_{11}H_{10}O_5$ should neutralise 0·0464:

0·1285 gave 0·2781 CO_2 and 0·0521 H_2O. C = 59·0; H = 4·51.

$C_{11}H_{10}O_5$ requires C = 59·5; H = 4·5 per cent.

The *calcium* salt is characteristic; it is much less soluble than the barium or potassium salt, and it crystallises in warts, of the composition $(C_{11}H_9O_5)_2Ca,3H_2O$. When heated it seems to decompose, for concordant figures for the water of crystallisation could not be obtained:

0·1857 gave 0·0472 $CaSO_4$. Ca = 7·48.
0·1598 „ 0·0402 $CaSO_4$. Ca = 7·40.

$(C_{11}H_9O_5)_2Ca,3H_2O$ requires Ca = 7·46 per cent.

The constitution of the acid is shown by the fact that it can be converted by a series of changes into the methyl ether of β-coccinic acid. Hence it is 5-methoxy-3-methylphthalide-2-carboxylic acid, and the isomeride produced at the same time must be 3-methoxy-5-methylphthalide-2-carboxylic acid.

5-*Methoxy*-3-*methylphthalide* (XIII β).

The phthalidecarboxylic acid of m. p. 170° (6 grams) along with naphthalene (20 grams) was heated at 180—190° until the evolution of carbon dioxide ceased. The residue was then distilled in a current of steam in order to remove naphthalene, care being taken not to continue the operation unduly, because the phthalide is somewhat volatile with steam. It crystallises from water or acetone in colourless needles or slender prisms, melting at 105·5°:

0·1068 gave 0·2636 CO_2 and 0·0554 H_2O. C = 67·3; H = 5·8.

$C_{10}H_{10}O_3$ requires C = 67·4; H = 5·6 per cent.

5-*Methoxy*-3-*methylphthalic Acid* (IV β).

The phthalide just described (3·2 grams) was dissolved in dilute potassium hydroxide solution, and to this was added a solution of potassium permanganate (3·8 grams) in water (100 c.c.). After about twelve hours the hydrated oxide of manganese was removed by filtration, and the filtrate was acidified and extracted with ether. The ethereal extract gave on evaporation a white solid, which was an acid; it was crystallised from acetic acid and then from water, when it melted and effervesced at 184°.

0·1306 neutralised 12·46 c.c. 0·1*N*-sodium hydroxide, or 0·04984 NaOH, whilst this amount of the dibasic acid, $C_{10}H_{10}O_5$, ought to neutralise 0·04975 NaOH:

0·1459 gave 0·3061 CO_2 and 0·0641 H_2O. C = 57·2; H = 4·9.

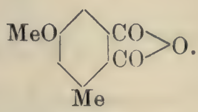
$C_{10}H_{10}O_5$ requires C = 57·1; H = 4·8 per cent.

For the purpose of comparison with the synthetic substance, the methyl ether of β-coccinic acid was prepared from cochenillic acid. Cochenillic acid (3 grams) was heated at 255—260° until the evolution of carbon dioxide ceased. The cold residue, which was crystalline, was dissolved in acetone, and the addition of benzene to the solution caused the formation of a brown precipitate, which was removed by filtration. The filtrate was evaporated, and the solution gave crystals which melted at 168° (m. p. of β-coccinic

anhydride 166—168°, Liebermann and Voswinckel). The yield was 1·4 grams.

In order to obtain the methyl ether of β-coccinic acid, the anhydride (1·4 grams) was dissolved in potassium hydroxide, and methylated by the addition of methyl sulphate (2 c.c.) in the usual way. The solution having been acidified and the acid product isolated by means of ether, the acid was crystallised from water and then again from ether. It melted at 179°, and had a yellow tinge. The identity of this substance with the synthetic product was tested by the "mixed melting-point" method. The synthetic product melted at 184°, and the mixture at 183°, the temperature being raised rapidly. It must be noted that this "melting-point" is really the temperature of rapid conversion of a phthalic acid into its anhydride, and can be altered, for instance, by altering the rate of heating.

5-*Methoxy*-3-*methylphthalic Anhydride*,



The anhydride was prepared by heating the phthalic acid very carefully. The product having been dissolved in hot benzene, it separated in wisps of needles.

0·1095, dissolved in water (50 c.c.), neutralised 11·37 c.c. 0·1*N*-sodium hydroxide solution, or 0·04548 NaOH, whilst this amount of phthalic anhydride, $C_{10}H_8O_4$, ought to neutralise 0·04562 NaOH.

The synthetic anhydride melted at 139°. There was only enough of the anhydride made from cochenillic acid for the "mixed melting-point" test. The mixture melted at 138°.

3-*Methoxy*-5-*methylphthalide*-2-*carboxylic Acid* (XII γ).

The trichloromethylphthalides having been hydrolysed, and the precipitated sodium salt separated, as described on p. 1717, the filtrate was treated with acid, so as to leave it faintly alkaline, and then boiled to remove alcohol. The solution was acidified, and the resulting precipitate was crystallised once from glacial acetic acid.

The material thus obtained is a mixture of two isomeric organic acids, and the separation of the two was carried out by means of the calcium salts. The mixture was dissolved in ammonium hydroxide, and then calcium chloride solution was added. First the calcium salt of 5-methoxy-3-methylphthalide-2-carboxylic acid separated in warts, and finally, from the concentrated mother

liquors, the calcium salt of 3-methoxy-5-methylphthalide-2-carboxylic acid in silky needles. The free acid obtained from this calcium salt is a white substance, which crystallises from acetone in short, stout, oblique prisms. For analysis it was crystallised from acetic acid and then from water. It melts at 190°.

0·1853 neutralised 8·36 c.c. 0·1*N*-sodium hydroxide solution, or 0·03344 NaOH, whilst this amount of the acid $C_{11}H_{10}O_5$ ought to neutralise 0·03339:

0·1355 gave 0·2928 CO_2 and 0·0553 H_2O. C=58·9; H=4·53.

$C_{11}H_{10}O_5$ requires C=59·5; H=4·5 per cent.

The *calcium* salt was analysed. As in the case of the calcium salt of the isomeric acid, concordant figures for the water of crystallisation were not obtained:

0·1779 gave 0·0440 $CaSO_4$. Ca=7·28.

$(C_{11}H_9O_5)_2Ca,3H_2O$ requires Ca=7·46 per cent.

3-*Methoxy*-5-*methylphthalide* (XIII γ).

3-Methoxy-5-methylphthalide-2-carboxylic acid (9 grams) along with naphthalene (27 grams) was heated at 180—190° until the evolution of carbon dioxide ceased. The naphthalene having been removed by distillation in a current of steam, the residue was crystallised from acetone, and then from alcohol, from which it separated in yellow, minute scales, melting at 135·5°:

0·1351 gave 0·3318 CO_2 and 0·0684 H_2O. C=67·0; H=5·6.

$C_{10}H_{10}O_3$ requires C=67·4; H=5·6 per cent.

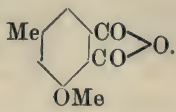
3-*Methoxy*-5-*methylphthalic Acid* (IV γ).

The phthalide just described (10 grams) was dissolved in potassium hydroxide solution, and then a solution of potassium permanganate (12 grams) in water (400 c.c.) was added. After about twelve hours the hydrated oxide of manganese was removed, the solution was rendered faintly alkaline, evaporated to small bulk, and acidified. The free acid was purified by crystallisation from glacial acetic acid, and then from acetone; it consists of colourless, minute crystals, and melts and effervesces at 200°.

0·0609 neutralised 5·82 c.c. 0·1*N*-sodium hydroxide solution, or 0·02328 NaOH, whilst this amount of the dibasic acid, $C_{10}H_{10}O_5$, ought to neutralise 0·02320:

0·1297 gave 0·2713 CO_2 and 0·0576 H_2O. C=57·05; H=4·9.

$C_{10}H_{10}O_5$ requires C=57·1; H=4·8 per cent.

3-Methoxy-5-methylphthalic Anhydride, 

The anhydride was prepared by carefully heating the corresponding phthalic acid. It crystallised from benzene in pale yellow needles, melting at 167°.

0·0992, dissolved in water (50 c.c.), neutralised 10·42 c.c. 0·1*N*-sodium hydroxide solution, or 0·04168 NaOH, whilst this amount of a phthalic anhydride, $C_{10}H_8O_4$, ought to neutralise 0·4133.

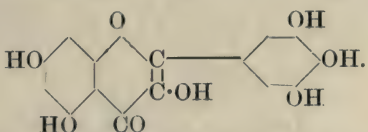
The author is grateful to the Executive Committee of the Carnegie Trust for the Universities of Scotland for a grant which largely defrayed the expenses of this investigation. He would also make grateful acknowledgment of the abundant facilities for original work which he enjoyed in the Chemical Department of Manchester University throughout his tenure of a Carnegie Research Fellowship.

Department of Organic Chemistry,
The University, Manchester.

CXCIII.—*Myricetin. Part III.*

By Arthur George Perkin.

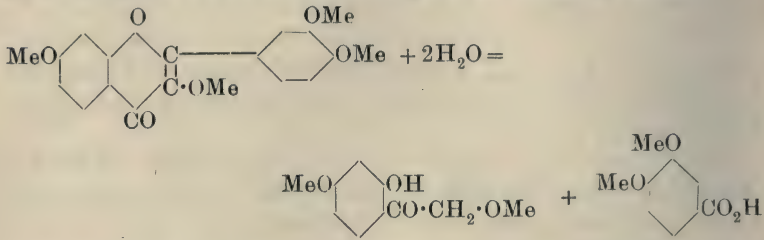
In previous communications (Trans., 1896, **69**, 1287; 1902, **81**, 203) it has been shown that myricetin possesses very similar properties to quercetin, and is most probably a hydroxy-derivative of the latter colouring matter. As on hydrolysis it yields phloroglucinol and gallic acid, the following constitution was assigned to this substance:



Owing to a lack of raw material, it was not possible at the time fully to establish this point, but having recently obtained through the kindness of Professor Kametaka, of Tokio, a large supply of an extract of *Myrica nagi* which has proved to give more than an average yield of the colouring matter, further experiments have been undertaken.

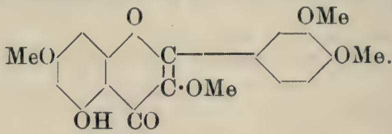
It has been shown by Herzig (*Monatsh.*, 1891, **12**, 187) that when

fisetin tetramethyl ether is digested with boiling alcoholic potassium hydroxide it is hydrolysed according to the following scheme:



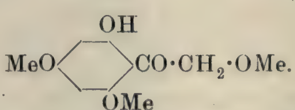
with formation of veratric acid and fisetol dimethyl ether, and, indeed, fisetin is the first compound to which a flavonol constitution was assigned.

When, however, quercetin tetramethyl ether, the fullest methylation product of quercetin which could be obtained by the employment of methyl iodide, was similarly treated (Herzig,



Monatsh., 1888, **9**, 552), veratric acid and a syrupy phloroglucinol derivative, subsequently identified as phloroglucinol monomethyl ether (Trans., 1902, **81**, 471), were produced. Myricetin pentamethyl ether behaved similarly, with production of gallic acid, trimethyl ether, and phloroglucinol monomethyl ether.

More recently it has been shown by Waliaschko (*Arch. Pharm.*, 1904, **242**, 242) that quercetin pentamethyl ether can be prepared by means of methyl sulphate, and Herzig (*Ber.*, 1909, **42**, 155) has now found that this completely methylated compound is hydrolysed by alcoholic potassium hydroxide in an analogous manner to fisetin tetramethyl ether, with production of veratric acid and *o*-hydroxyfisetol trimethyl ether (6-hydroxy-2:4-dimethoxyphenyl methoxymethyl ketone):



An interesting point in connexion with myricetin (*loc. cit.*) is the fact that, although methyl iodide gives only a pentamethyl derivative, ethyl iodide, on the other hand, furnishes the hexaethyl compound, for with other members of the flavonol group no fully ethylated derivatives have been hitherto produced by this method. During the previous investigation the action of alcoholic potassium

hydroxide on this compound was studied with unsatisfactory results, in that the anticipated hydroxyfisetol triethyl ether did not appear to be formed as a result of the hydrolysis. As, however, it seemed possible that the difficulty may have arisen from the fact that but a very meagre quantity of the myricetin hexaethyl ether was available for the experiments, or from a too prolonged action of the alkali, it was desirable to re-investigate this point with a larger quantity of the substance, and simultaneously to study the hitherto unknown myricetin hexamethyl ether in this respect.

Experimental.

The following method was employed for the preparation of myricetin from the *Myrica nagi* extract. Four hundred grams of the material were dissolved in 6 litres of hot water, the solution treated with 400 c.c. of hydrochloric acid (33 per cent.), and heated to the boiling point for two hours, in order to hydrolyse the glucoside myricitrin. When cold, the deep brown precipitate was collected, dried at the ordinary temperature, and extracted with alcohol. The extract, when evaporated to a small bulk and cautiously treated while hot with a little boiling water, became semi-solid, owing to the separation of crude myricetin, which was removed by filtration, and washed with dilute alcohol. Yield, 37 grams. For purification, and more especially with the object of removing a trace of a second colouring matter, probably quercetin, which is present, the product was acetylated, and the acetyl derivative crystallised from a mixture of acetic acid and alcohol until it melted at 211—212°. It was subsequently hydrolysed with acid in the usual manner, with the production of approximately 20 grams of pure myricetin.

Experiment indicated that myricetin hexamethyl ether can be readily prepared by treating the dry potassium salt of the pentamethyl compound with cold methyl sulphate. Waliaschko (*loc. cit.*) employed this method successfully in the preparation of quercetin pentamethyl ether from the trimethyl ether, and the same process with certain modifications was subsequently adopted by Watson (Proc., 1911, **27**, 163). The product of the reaction was washed with ether, digested with hot water, and crystallised from alcohol with the aid of animal charcoal.

On the other hand, myricetin can also be fully methylated by treating its solution in methyl alcohol with a large excess of alkali and methyl sulphate, as suggested by Herzig (*loc. cit.*) in the case of quercetin. On keeping, *myricetin hexamethyl ether* does not separate, but is gradually deposited when the concentrated alcoholic solution is diluted with water.

Found: C=62·69; H=5·30; Me=21·96.

$C_{15}H_4O_2(OMe)_6$ requires C=62·68; H=5·47; Me=22·38 per cent.

When slowly crystallised from alcohol it separates in prismatic needles, but by rapidly cooling the hot concentrated solution, as a colourless, woolly mass of fine needles resembling quercetin pentamethyl ether. It melts at 154—156°, and is sparingly soluble in cold alcohol.

In order to study the products of the hydrolysis of myricetin hexamethyl ether, 5 grams of the substance were digested with a boiling solution of 10 grams of potassium hydroxide in 50 c.c. of 80 per cent. alcohol for seven hours. The hot liquid, which on cooling became semi-solid owing to the separation of a potassium salt, was evaporated to dryness, treated with water, and the solution filtered from a trace of insoluble matter. On passing carbon dioxide into this solution, colourless crystals separated in considerable amount, and when these had been removed (2·18 grams), the filtrate yielded to ether a further quantity of the same compound (0·34 gram). It was purified by crystallisation from alcohol. (Found, C=58·36; H=6·39; Me=19·45. Calc., C=58·41; H=6·19; Me=19·91 per cent.) It consisted of colourless, prismatic needles, and appeared to be identical with the *o*-hydroxyfisetol trimethyl ether which Herzig obtained from quercetin pentamethyl ether, in that it melted at 102—104°, and the oxime which was prepared from it at 146—148°.

Being in possession of some quercetin tetramethyl ether, this was converted into the pentamethyl compound by Waliaschko's method (an operation which proceeds quite as smoothly as when the trimethyl ether is employed), and from this hydroxyfisetol trimethyl ether was prepared. A mixture of this substance and that produced from myricetin hexamethyl ether melted at 102—104°. The mother liquors obtained when the crude hydroxyfisetol trimethyl ether was crystallised from alcohol contained a trace of a second compound, which could be only isolated as a viscid, readily soluble mass, and apparently consisted of crude phloroglucinol dimethyl ether.

The sodium bicarbonate solution from which the hydroxyfisetol trimethyl ether had been isolated gave, on neutralisation with acid, a colourless, crystalline precipitate (2·05 grams), and when this had been removed the filtrate yielded to ether a small quantity of the same substance (0·401 gram). It crystallised from water in needles, melting at 167—169°, and consisted of gallic acid trimethyl ether. (Found, C=56·64; H=5·57. Calc., C=56·61; H=5·66 per cent.) These results therefore rendered it fairly evident that myricetin hexaethyl ether should, when hydrolysed with boiling alcoholic potassium hydroxide under suitable conditions, yield, not only the

gallic acid triethyl ether previously obtained (*loc. cit.*), but also a hydroxyfisetol triethyl ether corresponding with the methyl compound above described.

Myricetin hexaethyl ether was prepared by treating a boiling solution of 14·5 grams of myricetin in 200 c.c. of alcohol and 70 c.c. of ethyl iodide with 28 grams of potassium hydroxide in alcohol drop by drop during two days. The product isolated as usual consisted of the almost pure ether (9·6 grams), which, after recrystallisation, melted at 149—151°.

When submitted to the action of boiling alcoholic potassium hydroxide under identical conditions to those employed with the methyl compound, myricetin hexamethyl ether yielded a solution which, when evaporated, gave a residue soluble in water. On passing carbon dioxide into the solution, a crystalline precipitate separated in considerable amount, and this, after being collected and crystallised from alcohol, was obtained in colourless, prismatic needles, melting at 96—97°. The analyses of this compound indicated that it had, as was anticipated, the composition of a *hydroxyfisetol triethyl ether*.

Found: C = 62·66, 62·49; H = 7·87, 7·61.

$C_{14}H_{20}O_5$ requires C = 62·68; H = 7·46 per cent.

The alcoholic mother liquors resulting from the purification of this compound contained a second product isolated as a transparent, viscid mass, which probably consisted of impure phloroglucinol diethyl ether. It is accordingly evident that the hydroxyfisetol triethyl ether to some extent suffers hydrolysis in the presence of boiling alcoholic potassium hydroxide, and the unsuccessful attempt to prepare it from myricetin hexaethyl ether in the former experiment can be therefore accounted for by the too prolonged action of the reagent.

As the result of this investigation there can be no doubt that myricetin is a hydroxyquercetin, and possesses the constitution given at the commencement of this paper. An attempt is in progress to synthesise myricetin by the employment of the degradation products of its hexamethyl ether (hydroxyfisetol trimethyl ether and gallic acid trimethyl ether), and the results of this work will, it is hoped, be shortly communicated to the Society.

CLOTHWORKERS RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS.

CXCIV.—*The Photochemical and Thermal Interaction of Chlorine and Carbon Monoxide.*

By David Leonard Chapman and Frank Houghton Gee.

In previous communications published by one of us in conjunction with C. H. Burgess and P. S. MacMahon on the photochemical interaction of chlorine and hydrogen, it has been postulated that the agency whereby the union of the gases is brought about is the evanescent forms of energy acquired by the molecules of the system from the visible light extinguished by the chlorine in virtue of the selective absorption exhibited by that gas. That the extinction of visible light by a sensitive mixture of chlorine and hydrogen is not greater than that resulting from the selective absorption of the chlorine, and that therefore the so-called photochemical extinction is an imaginary phenomenon, has been established by experiment (Burgess and Chapman, Trans., 1906, **89**, 1433). As this experimental result is of fundamental importance, so far as the theory of photochemical change is concerned, we may draw attention to the fact that Winther in his recent interesting work on Eder's solution (*Zeitsch. wiss. Photochem.*, 1910, **8**, 242) arrives at a similar conclusion. After conducting an experimental investigation on the point in question, he remarks: "Nach diesem Ergebnisse, mit den Resultaten von Burgess and Chapman (für chlorknallgas) und von Lemoine (für Ferrioxalat) zusammengehalten, scheint mir der Begriff der photochemischen Extinction, in seiner bisherigen Bedeutung aus der wissenschaftlichen Photochemie ausscheiden zu müssen." Concerning the mechanism of the photochemical changes under consideration, our own view is briefly this. Chlorine, when it is absorbing light, preserves, for a time, the transformed light energy in efficient forms which are gradually changed, and finally become the ordinary heat energy of the system, the rate of degradation being considerably greater in the presence of certain impurities. This efficient energy confers on the gas the property of reacting with other substances for which it possesses an affinity, and therefore the presence of those impurities which hasten the degradation of energy is a circumstance that can only result in a reduction in the rate of a possible photochemical change.

It might be urged that if efficient energy is accumulated in the chlorine in the manner assumed, and that if consequently the light is not instantly degraded to the state in which it exists in the unilluminated system at the same temperature, it ought to be possible to demonstrate the existence of this energy in the illumin-

ated gas by some physical means. The work of R. W. Wood on the resonance spectra of the elements would appear to have a direct bearing on this aspect of the question. Five years ago it was shown by this investigator that iodine—an element allied to chlorine—in the state of vapour emits a green light when the rays from an arc lamp act on it, and that in the presence of small quantities of oxygen the fluorescent light is considerably reduced in intensity. At that time an unsuccessful attempt was made to show that chlorine would fluoresce under similar conditions. Quite recently Wood has returned to the subject (*Phil. Mag.*, 1911, [vi], **21**, 261, 309, and 314), and his latest results are such as to strengthen the conviction that there is a close relationship between the phenomena investigated by him and those observed in the study of photochemistry. He has now shown that, when the pressure is sufficiently low, bromine vapour can be made to fluoresce, a fact which very considerably increases the probability that chlorine, exposed to light rays, will ultimately be shown to be capable of retaining the absorbed energy in an efficient form for a sufficient length of time to give rise to the phenomenon of fluorescence. What is still more significant is the influence of impurities on the fluorescence of iodine vapour. When the vapour is excited by monochromatic light—the green line of mercury—and the fluorescent light is analysed, it has been found to consist of a number of lines, designated by Wood a resonance spectrum. The line spectrum becomes a band spectrum when helium is present in the vapour, and at the same time the proportion of light in the red to that in the green is increased. The helium transforms and simultaneously degrades the energy. Wood also finds that after the iodine vapour has been mixed with the electronegative gases chlorine or oxygen, the degradation is so rapid that the fluorescence can no longer be made manifest. Now all the gases which retard or prevent the interaction of chlorine and hydrogen are likewise electronegative in character. This close coincidence would be most remarkable if merely fortuitous, but if, as we are disposed to think, it arises from a causal connexion between the two classes of phenomena, it could scarcely be disputed that it does afford strong presumptive evidence in favour of the view that photochemical inhibition results from the property possessed by the inhibitor of degrading the energy essential to the progress of the chemical change. The fact (for which this communication contains evidence) that the gases which behave as inhibitors towards the action between chlorine and carbon monoxide are also inhibitors in the case of the interaction of chlorine and hydrogen, lends further support to the same view.

We may here offer a few remarks on the views published by

Weigert (*Ann. Physik*, 1907, [iv], **24**, 55 and 243) on the mechanism of photochemical changes. Weigert finds that although visible light hastens both the decomposition of carbonyl chloride and the combination of chlorine and carbon monoxide at temperatures ranging between 450° and 510°, it is incapable of altering the percentage composition of a mixture of chlorine, carbon monoxide, and carbonyl chloride in thermal equilibrium. Basing his views on this fact, he argues that the action of the light is merely catalytic in its nature, and he maintains that there is produced, under the action of light, a catalyst in the form of molecular complexes ("Reaktionskerne"), the influence of which on the chemical change may be compared with that of the microscopic particles of platinum in a colloidal solution of that metal on the decomposition of hydrogen peroxide. The theory does not commend itself to us for two reasons, which are: (*a*) the want of any independent evidence for the existence of reaction nuclei in the illuminated system, (*b*) its necessary limitation, in its present form, to that class of photochemical changes in which there is no accumulation of available energy. Coehn and Becker (*Ber.*, 1910, **43**, 130) have shown that carbonyl chloride is appreciably decomposed into chlorine and carbon monoxide by the very refrangible ultraviolet rays emitted by a quartz mercury lamp, at a temperature considerably below that at which the concentration of the products of dissociation of carbonyl chloride in thermal equilibrium with the vapour of carbonyl chloride is sufficiently great to be capable of being measured, and they have pointed out that the statement on which Weigert bases his views that the equilibrium between carbonyl chloride and its products of decomposition is uninfluenced by light, is not therefore generally true. We are not aware, however, of any ascertained facts connected with the union of chlorine with hydrogen or carbon monoxide in visible light actually inconsistent with Weigert's hypothesis, which may consequently be still held as an alternative explanation of a limited class of photochemical changes.

For the investigation of some questions the action between chlorine and carbon monoxide possesses advantages over that between chlorine and hydrogen. The union of the former gases is accompanied by a contraction, and therefore the course of the change can be followed without water being present. The absence of water, besides making it possible to perform experiments at high temperatures, is also a distinct advantage in the investigation of the effects of those inhibitors which dissolve in, or are acted on by, this liquid. Thus, owing to the solubility of nitrosyl chloride in water, the influence of this inhibitor on the photochemical interaction of chlorine and hydrogen could not be investigated so

completely as was desirable, whereas with a mixture of chlorine and carbon monoxide it has been found possible to demonstrate that a small quantity of nitrosyl chloride not only—as with a mixture of chlorine and hydrogen—prevents almost entirely the combination of the gases under the influence of light, but, like oxygen and unlike nitrogen chloride exerts its influence without itself undergoing change. On the thermal union of chlorine and carbon monoxide the influence of nitrosyl chloride is inappreciable, a fact completely in agreement with the views that we hold on the nature of photochemical change. It was, in fact, mainly with the object of testing the latter consequence of our theory that the present investigation was undertaken.

Experimental.

In the preliminary experiments the actinometer was the same in construction as that used by Burgess and Chapman in the experiments on chlorine and hydrogen. The methods of controlling the temperature, of keeping the pressure at the open end of the index constant, and of adding measured volumes of foreign gases, were also the same as those adopted in previous investigations.

The chlorine was prepared from manganese dioxide and hydrochloric acid, and hydrogen chloride was removed from the gas by its being bubbled through previously boiled chlorine water. The manganese dioxide was digested for several hours with chlorine water, and the hydrochloric acid was made (with the precautions observed by Chapman and MacMahon) by dissolving hydrogen chloride (from pure sodium chloride and concentrated sulphuric acid) in dilute chlorine water which had been previously boiled for a long time in a large flask provided with a ground-in reflux condenser. The carbon monoxide was prepared from sodium formate and concentrated sulphuric acid, and was washed with potassium hydroxide solution. The mixture of equal volumes of chlorine and carbon monoxide was made (with special precautions to exclude air) in a glass gas-holder containing concentrated sulphuric acid which had been previously saturated with chlorine and boiled. In spite of all the precautions taken to destroy unstable inhibitive substances, the mixture of gases prepared by the above method exhibited a short "induction period" on exposure to light. This was not, however, a serious disadvantage in the preliminary experiments.

The Inhibitive Influence of Nitric Oxide.—The filling of the actinometer with the mixture of chlorine and carbon monoxide was accomplished by preliminary substitution of dry chlorine for the air in the insolation vessel, and subsequent displacement of the chlorine with a sensitive mixture of the gases. The actinometer

was illuminated with a 32 c.p. incandescent lamp placed at a distance of about 25 cm. from the insolation vessel. The distances in centimetres traversed by the boundary of the sulphuric acid in the index-tube in successive intervals of 2 minutes are recorded below:

Time in minutes.	Movements of index.
2	−0·70 cm.
4	1·80 ,,
6	3·20 ,,
8	3·40 ,,
10	3·40 ,,
12	3·20 ,,
14	3·40 ,,

It will be observed that there was a short induction period. 0·3 Per cent. by volume of nitric oxide was then introduced into the insolation vessel, which, after being left for a short time in the dark, was again exposed to the rays of the lamp. The index remained quite stationary, and even after a period of two days it had not moved. The shutters of the window in the darkened room were then thrown open. The window faces the north, and the sky at the time was rather dull. The daylight failed to bring about a noticeable combination of the gases. A carbon arc lamp fed with a current of ten amperes was then placed as close to the insolation vessel as the bath in which the latter was contained would permit. In this intense light a slow combination of the gases, corresponding with a movement of the index of 0·21 cm. in a minute, was observed. The insolation vessel was exposed to the arc lamp for different periods of time, amounting in all to twenty-four hours, and the rate of movement of the index meanwhile fell to 0·18 cm. per minute, the fall being obviously due to the gradually decreasing partial pressures of the chlorine and carbon monoxide. Nitrosyl chloride is accordingly a very powerful inhibitor, and like oxygen is not removed from the system by the action of light.

The Inhibitive Influence of Ozone and of Nitrogen Chloride:—When mixtures of equal volumes of chlorine and carbon monoxide containing small quantities of ozone or nitrogen chloride were exposed to light, the occurrence of marked "induction periods" was observed. Ozone, being comparatively very unstable in the presence of chlorine, completely disappears from the mixture in a few hours. It was noticed that when nitrogen chloride was passed into the insolation vessel which contained the active mixture, a white deposit was formed on the inner surface of the glass. The character of this deposit has not yet been investigated. In its formation a considerable proportion of the nitrogen chloride must have been removed, and this would probably account for the fact that the observed "induction periods" were considerably shorter

than our knowledge of the effect of the same inhibitor on the union of chlorine and hydrogen had led us to expect.

The Inhibitive Influence of Oxygen:—The addition of even a small quantity of oxygen to an active mixture diminishes the sensitiveness considerably, but the fall in the sensitiveness effected by this means is not so great as that observed when a mixture in equivalent proportions of chlorine and hydrogen is subjected to the same treatment. It is possible that the sole cause of this difference is to be sought in the unequal degrees of freedom from initial contamination by oxygen of the respective mixtures. The electrolysis of concentrated hydrochloric acid, conducted with the precautions recommended by Bunsen and Roscoe, undoubtedly provides us with a means of preparing electrolytic gas contaminated with a smaller proportion of air than a mixture of chlorine and carbon monoxide, prepared by the method adopted in these experiments, contains.

It was owing to the circumstance that a mixture of chlorine and hydrogen can be obtained so free from inhibitive impurities that it was possible to show that the relation expressed by the equation:

$$[O] \times S = K$$

(in which $[O]$ is the concentration of the oxygen, S is the sensitiveness, and K a constant) holds approximately for small concentrations of oxygen (Chapman and MacMahon, Trans., 1909, **95**, 959). The same relation may be valid for a mixture of chlorine and carbon monoxide in equivalent proportions when the relative quantity of oxygen present in the mixture is small. The relation does not hold, however, when the oxygen is increased in amount. This will be made evident by an inspection of the following results furnished by the first experiment performed on this point.

Experiment I.

Oxygen introduced.	Sensitiveness.	$[O] \times S$.
Original mixture	4·30	—
1·6 per cent.........................	1·60	2·56
4·8 ,, ,, ...	1·24	5·95

When the magnitude of $[O]$ exceeds 1·5 per cent., the value of the product $[O] \times S$ rises rapidly as the oxygen is further increased. From the above results it would appear to be probable that the sensitiveness approaches a limit as the percentage of oxygen is increased. To test this conjecture, the following experiment was performed. The actinometer was filled with a mixture of equal volumes of chlorine and carbon monoxide at a pressure of half an atmosphere. Oxygen was then admitted until its partial pressure was one quarter of an atmosphere, and, after the sensitive-

ness had been measured, another equal quantity of oxygen was introduced, and the sensitiveness again taken. The results are recorded below.

Experiment IIa.

Oxygen introduced.	Sensitiveness.
25 per cent.	0·745
50 ,, ,, ...	0·733

Below are the results furnished by a second experiment performed in the same way.

Experiment IIb.

Oxygen introduced.	Sensitiveness.
25 per cent.	0·763
50 ,, ,, ...	0·733

In order to discover whether the value of the product $[O] \times S$ approaches a limit as the amount of oxygen in the mixture is reduced, an experiment was performed in which the value of the sensitiveness of mixtures containing smaller amounts of oxygen was measured.

Experiment III.

Oxygen introduced.	Sensitiveness.	$[O] \times S$.
0·44 per cent.	2·01	0·8844
0·88 ,, ,, ...	1·32	1·1616
1·76 ,, ,, ...	0·84	1·4784
3·52 ,, ,, ...	0·56	1·9712

A comparison of the results of all the experiments discloses a manifest tendency of the product $[O] \times S$ to approach a limiting value as the amount of oxygen is reduced, and this tendency would be still more apparent if a correction were made for the small amount of oxygen contained in the original mixture. The values for the sensitiveness in the experiments I, II, and III are not comparable, since light of different intensities had to be employed in the separate experiments in order that the rates of combination might have the most convenient magnitudes.

It would appear that, as a first approximation, the sensitiveness of a mixture of chlorine and carbon monoxide in equivalent proportions containing oxygen at different partial pressures is given by the formula:

$$S = A + B/[O],$$

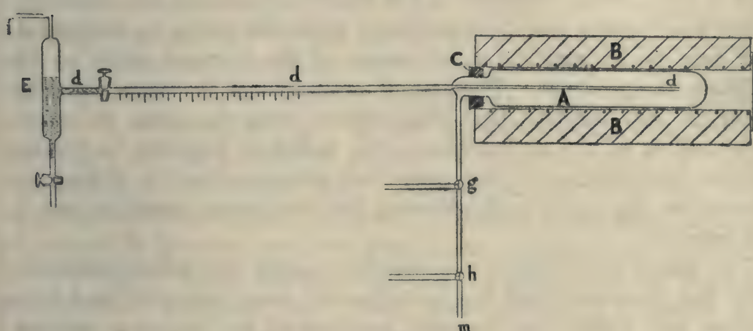
in which A and B are constants and S and $[O]$ have the same significance as before. If $[O]$ is small, S is so large that, in comparison, A becomes negligible; but if $[O]$ is large, S becomes almost equal to A. That the sensitiveness of the mixture is independent of the partial pressure of the oxygen when the value of the latter is large, would seem to indicate that the effective energy is not homo-

geneous in character, and that in the degradation of certain forms of it, which constitute a small fraction of the whole, the oxygen plays a less important part than the other substances present in the mixture.

Experiments at Higher Temperatures.

The apparatus was designed so as to admit of the insolation vessel being heated and at the same time exposed to light. Fig. 1 is a diagrammatic representation of the actinometer. The insolation vessel *A* was enclosed in the porcelain tube of the electric resistance furnace *B*. One end of the porcelain tube was closed with the asbestos stopper *C*, and the other end with the transparent mica plate *D*, through which the light was admitted to the insolation vessel. The index tube *d* communicated with the reservoir *E*,

FIG. 1.



which contained sulphuric acid. The glass tube *f* at the top of *E* was connected to a large glass bottle, the air in which could be kept at any desired pressure. The current supplied to the furnace was regulated by an ammeter and an adjustable resistance. The gases were admitted to the insolation vessel through the tube *m*. As the actinometer could be partly or completely exhausted through the index tube *d*, and the pressure measured by a manometer connected with the large bottle mentioned above, but not shown in the figure, the filling with a mixture of known composition could be accomplished by admitting the gases separately to the insolation vessel. Before filling the actinometer, the air was driven out of it with a current of chlorine. The three-way taps *g* and *h* served the same purpose as formerly (Chapman and MacMahon, Trans., 1909, **95**, 961).

For the earlier experiments a mixture of chlorine and carbon monoxide prepared as described above was used. It was found

that when the current heating the electric furnace was 2·35 amperes, corresponding with a temperature of 350°, the rate of union of the gases was conveniently rapid. We were surprised to find that the rates of interaction in the dark and in the light were almost the same at this temperature. The insolation vessel was alternately illuminated and shaded during intervals of time, each of four minutes' duration, and the position of the index at the end of every interval recorded. The mean rates of movement in the light and in the dark were:

Insolation vessel illuminated.	Insolation vessel shaded.
6·56 cm. in 2 minutes.	6·51 cm. in 2 minutes.

The source of illumination was an incandescent lamp of about 50 c.p. placed at a distance of 7 cm. from the mica window of the furnace.

In order to test if this unexpected result was due to the formation of some stable inhibitor at the high temperature, the insolation vessel was rapidly cooled immediately after the above measurements had been made, and the sensitiveness of the mixture taken at the ordinary temperature. The rate of movement of the index exceeded 8 cm. in two minutes, the illumination being the same as before. The cooling of the actinometer with sufficient rapidity to prevent further combination of the gases was accomplished by sliding the furnace to the right, and allowing the insolation vessel to cool in the open air.

The above experiment was repeated under the same conditions, with the exception that the incandescent lamp was displaced by a carbon arc, which was brought quite close to the mica window. The following measurements were obtained at the high temperature:

Insolation vessel illuminated.	Insolation vessel shaded.
7·35 cm. in 2 minutes.	6·66 cm. in 2 minutes.

The rate at which the gases in the insolation vessel combined after they had been cooled and then exposed to the same light was too rapid to admit of a measurement being made. The experiment was repeated several times, and always gave the same result. The mixture became insensitive to light at the higher temperature, and recovered its sensitiveness on being cooled. A short preliminary account of the phenomenon just described has been communicated (Proc., 1911, **27**, 56), and it was therein stated that the experiments were being performed over a wider range of temperature. As the experiments in question have failed to elicit the information which we hoped to obtain from them, a brief general account of such of them as have furnished knowledge required in the subsequent investigation of other questions will suffice.

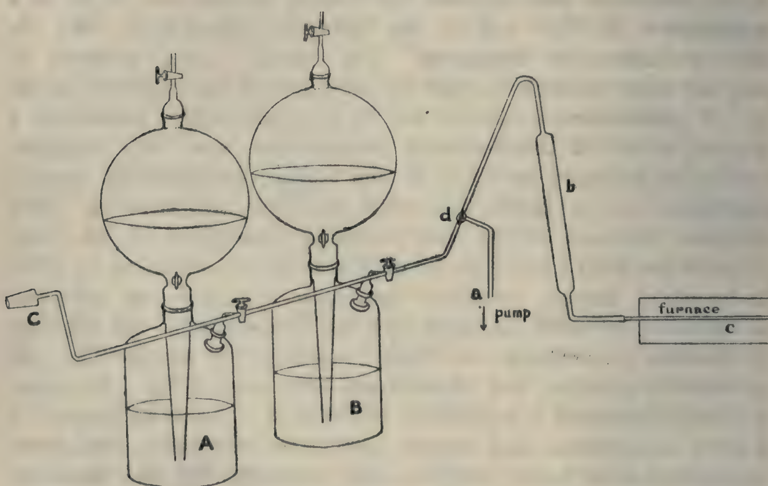
The Photochemical Interaction of Chlorine and Carbon Monoxide at 170°.

From the result of the foregoing experiment it might not unreasonably be expected that the temperature-coefficient of the rate of photochemical interaction of chlorine and carbon monoxide would be found to have a value less than unity. It is known that at the ordinary temperature photochemical changes, unlike spontaneous changes, are scarcely affected by a change of temperature of a few degrees. This was observed by Bunsen and Roscoe to be the case for the union of chlorine and hydrogen, and has since come to be regarded as the general rule. In order to obtain information on this interesting point, mixtures of chlorine and carbon monoxide were exposed successively to the same light at a temperature of 172° and at the ordinary temperature, and the rates of interaction compared. The results were, however, so irregular that attempts to find the influence of temperature on the rate of photochemical change had to be abandoned. Sometimes a mixture which at the ordinary temperature was very sensitive would, on exposure to light at the higher temperature, remain unchanged for an indefinite period of time, whereas, on other occasions, mixtures which were relatively insensitive at the lower temperature would prove to be only a little less sensitive at 172°. At length it became manifest that some impurity—an inhibitor the efficiency of which increases with the temperature—was affecting the results. Although we have endeavoured to identify the inhibitor in question, our efforts have been unavailing. We have, however, elaborated a process by which it is possible to prepare a mixture of chlorine and carbon monoxide sufficiently free from contamination with the objectionable impurity for the principal object we had in view. In this process oxygen is also almost completely eliminated, and the mixtures obtained are accordingly extremely sensitive. In Fig. 2 the essential parts of the apparatus used in the process are depicted.

The two gas-holders *A* and *B* contained water which had been thoroughly digested with chlorine, the use of sulphuric acid for confining the gases having been found to be unsatisfactory. The gas-holder *A* contained the carbon monoxide and the holder *B* the chlorine, the water in *B* having been, of course, saturated with the gas it was to contain. The ground-glass stopper *C* fitted into a long-necked flask, in which the gases were separately prepared. The air was removed from this flask by means of a pump connected to the tube *a*. The tube *b* was filled with fused calcium chloride. The further end of *b* communicated directly with a long quartz tube *c*,

surrounded by a furnace which could be raised to a temperature of about 1000°. The gases passed from *c* through a glass capillary tube into the insolation vessel. The whole apparatus between *d* (Fig. 2) and *h* (Fig. 1) could be exhausted through the tap *h*. After the gas-holders *A* and *B* had been filled with carbon monoxide and chlorine respectively, a small volume of chlorine was passed from *B* into *A*, and an equal volume of carbon monoxide from *A* into *B*. *A* then contained carbon monoxide mixed with about 1 per cent. of chlorine, and *B* contained chlorine mixed with the same percentage of carbon monoxide. The impurities capable of giving rise to an "induction period" were destroyed with the aid of the chlorine as the gases passed through the heated quartz tube *c*. At

FIG. 2.



the same time any oxygen present in the gases from either of the holders was almost entirely eliminated by its entering into combination with the carbon monoxide present.* The gases were, of course, separately admitted to the actinometer. All the glass taps were lubricated with glacial phosphoric acid.†

* At 600° and at atmospheric pressure, the dissociation of carbonyl chloride is approximately 90 per cent. ; at 1000° it would be almost complete, whereas at the same temperature and pressure carbon dioxide is dissociated to the extent of only 0·004 per cent.

† The viscous fluid formed on the surface of a stick of glacial phosphoric acid, which has been exposed for a short time to the air and then kept in a dry atmosphere for some time, is a better lubricant for glass taps than phosphoric oxide which has been permitted to become moist. The lubricant formed from the oxide generally contains solid particles which, besides being in themselves a disadvantage,

It was found that if the mixture of chlorine and carbon monoxide was made from carbon monoxide which had been quite recently prepared, its sensitiveness to light fell rapidly as the temperature rose, whereas a mixture made from carbon monoxide which had been kept in the presence of water for several days was relatively much more sensitive at the higher temperatures. Under no conditions, however, have we ever been able to obtain a mixture which was not many times less sensitive above 300° than at the ordinary temperature.

The Influence of Nitric Oxide and of Oxygen on the Thermal and Photochemical Interaction of Chlorine and Carbon Monoxide.

With chlorine and carbon monoxide prepared and treated in the manner described above, the following experiments were performed. The insolation vessel was filled with chlorine and heated for an hour at a temperature just below the softening point of glass. The actinometer was then exhausted, and the temperature of the furnace lowered to 315°. As soon as the temperature of the insolation vessel had become constant, chlorine was permitted to enter in a regular stream until the pressure had reached half an atmosphere. Carbon monoxide was then passed into the actinometer until the pressure was that of an atmosphere. The filling of the actinometer was accomplished in ten to fifteen minutes. Very shortly after the actinometer had been filled, the rate of movement of the index was recorded. It was 12·70 cm. in eight minutes, that is, 1·59 cm. per minute. An arc lamp was then placed at a distance of 25 cm. from the mica window of the furnace, and, with the insolation vessel exposed to, and shaded from, the light alternately for intervals of four minutes' duration, readings of the rate of movement of the index were taken. The means of the two series of readings were:

In the dark.	In the light.
1·66 cm. per minute	2·72 cm. per minute.

When the source of light was moved much closer to the mica window the rate of movement of the index increased to 5·65 cm. per minute. Incidentally, it may be mentioned that it is known from the results of other experiments that if the mixture had been rapidly cooled and then exposed to the same light at the ordinary temperature, the rate of movement of the index would have been too rapid to admit of a measurement being made. A small volume

facilitate the diffusion of atmospheric moisture into the space between the stopper and the barrel. A tap lubricated with glacial phosphoric acid will hold for weeks without the precaution being taken of protecting the lubricant from the action of the moisture of the air by an external coating of grease.

of nitric oxide was immediately admitted to the insolation vessel, and measurements of the rate of movement of the index in the light again made, the arc lamp being in its former position. The rate of movement of the index fell a little below that recorded for the thermal combination before the nitric oxide had been admitted, the actual value being 1·55 cm. per minute. The rate of movement of the index in the dark had precisely the same value. The presence of nitrosyl chloride therefore prevents the mixed gases from responding to light stimulus, but does not hinder their thermal interaction. The inhibitive effect of nitrosyl chloride is restricted to the photochemical change. The above experiment was repeated several times, the result being the same on every occasion.

It has been shown that, within the limits of accuracy attainable, oxygen is without catalytic influence on the pyrogenic union of chlorine and carbon monoxide. This was demonstrated by admitting oxygen to the actinometer whilst combination was proceeding, and observing that the rate of movement of the index did not alter. It is also evident that the effect of oxygen, if any, on the pyrogenic union of the gases must be negligible in comparison with its powerful influence on the photochemical change from the circumstance that the initial rate of pyrogenic union of chlorine and carbon monoxide has always practically the same value, at the same temperature, for mixtures of the gases in equal volumes, although the proportion of oxygen contained in mixtures prepared at different times must be very variable.

The Homogeneity of the Thermal Interaction of Chlorine and Carbon Monoxide:—In the study of spontaneous changes in gases, the first point to be ascertained before any conclusions of theoretical interest can be drawn is whether or not the observed change is mainly homogeneous. This point has accordingly been investigated in the present case, and, from the results of the experiments undertaken with this object in view, we conclude that the thermal union of chlorine and carbon monoxide under the conditions prevailing throughout this research may for all practical purposes be regarded as homogeneous in character. The experiments which establish this result are detailed below.

The insolation vessel of the actinometer was filled as rapidly as possible with a mixture of chlorine and carbon monoxide in the manner described above, and the rate of movement of the index during an interval of twenty minutes observed. The rate was 1·755 cm. per minute. The insolation vessel was then cooled, the furnace removed, and a hole fused in the end of the insolation vessel with the blow-pipe. Through this hole six grams of

thoroughly cleansed glass wool were introduced in such a manner as to fill the tube almost completely. The hole through which the glass wool had been introduced was then closed. The furnace was replaced, and the insolation vessel again raised to the temperature of 315°, dry chlorine being meanwhile slowly passed through it. The actinometer was then filled as before, and the initial rate of combination of the chlorine and carbon monoxide determined. The mean rate of movement of the index, taken as previously over a period of twenty minutes, was 2·226 cm. per minute. In order to compare this rate with that found when the actinometer contained no glass wool, an allowance must be made for the decreased volume of the gas. After making this correction, the following ratio was calculated:

$$\frac{\text{Rate with actinometer filled with glass wool}}{\text{Rate with actinometer empty}} = 1{\cdot}237$$

The ratio of the surface of the glass in contact with the combining gases in the last experiment to that in the first experiment was estimated to be 23·3.

It is manifest from these numbers that glass is only a weak catalyst for the change:

$$CO + Cl_2 \rightleftharpoons COCl_2,$$

and that in our experiments the thermal union of chlorine and carbon monoxide may for all practical purposes be regarded as a homogeneous change.

General Conclusions.

(1) In glass vessels the thermal interaction of chlorine and carbon monoxide is almost entirely homogeneous if the surface of the glass is not exceptionally large.

(2) The photochemical change is retarded, and in some cases almost entirely prevented from taking place, by small quantities of certain gases and vapours.

(3) The rate of the thermal change is not appreciably affected by the presence of small amounts of these inhibitors.

SIR LEOLINE JENKINS LABORATORIES,
JESUS COLLEGE, OXFORD.

CXCV.—*The Reactivity of Ketones towards Iodine and the Relative Rates of Tautomeric Change. Part II.*

By Harry Medforth Dawson and Harry Ark, M.Sc.

In continuation of previous experiments on the relative rates of tautomeric change of ketones (Dawson and Wheatley, Trans., 1910, **97**, 2048) as measured by the velocity with which they react with iodine under the catalytic influence of a mineral acid, the authors have carried out a further series of measurements in which certain dialkyl ketones and substituted acetophenones were investigated.

As in the earlier series, the kinetic measurements were made at 25° in an aqueous-alcoholic solution containing 40 volumes per cent. of ethyl alcohol with 0·1 molar sulphuric acid as catalyst. When the ketone present in the solution is such that its concentration remains sensibly constant during the period in which the progress of the reaction is followed, the tautomeric change of the ketone proceeds, under normal conditions, with constant velocity, which is measured by the rate of disappearance of iodine added as indicator.

In pure aqueous solution it is necessary to add a small quantity of an iodide in order to bring the requisite amount of iodine into solution. Although the solubility of iodine in 40 per cent. alcohol is such that the addition of iodide is not absolutely necessary, the earlier measurements were, as a matter of fact, made with solutions which contained small quantities of potassium iodide in order to diminish errors resulting from the volatility of the free iodine. For many ketones the reaction proceeds in exactly the same way and at the same rate, whether potassium iodide is present or not, but this is not always the case.

In the estimation of the enolised ketone a measured volume of the solution was added to a slight excess of sodium acetate in order to destroy the catalytic action of the mineral acid, and the resulting solution was then titrated with a freshly prepared 0·1*N*-sodium thiosulphate solution. In the case of methyl *iso*propyl ketone and pinacolin, it was observed that the end-point was very ill-defined, and that the blue colour of the starch-paste returned very quickly. This pointed to the liberation of iodine from the iodide present in the solution, and blank tests, in which the ketones were added to an acidified solution of potassium iodide, showed that iodine was liberated in considerable quantity and at a rapid rate. Liberation of iodine from the iodide was also observed with benzyl methyl

ketone, dibenzyl ketone, deoxybenzoin, and methyl *iso*butyl ketone, although the quantity set free and the speed of the reaction were much smaller than in the case of methyl *iso*propyl ketone and pinacolin.

The nature of this disturbing reaction has not been more closely examined, and it is not yet known whether it is of the same kind in all cases. It seems probable that the liberation of iodine in solutions of dibenzyl ketone is connected with the oxidation of this substance by atmospheric oxygen (Fortey, Trans., 1899, **75**, 871), whereby phenylacetic acid and benzaldehyde are produced. In consequence of the further oxidation of the aldehyde, iodine will then be set free from the iodide (compare Baeyer and Villiger, *Ber.*, 1900, **33**, 1569).

In consequence of this liberation of iodine from iodides by certain ketones, it was necessary, in such cases, to eliminate the iodide from the solutions employed in the dynamic measurements. This reduces the disturbing effect to a very large extent, but does not entirely eliminate it, for, as the iodine disappears by combination with the enolised ketone, it is replaced by an equimolecular quantity of hydrogen iodide, from which iodine will be again set free to some extent by the action of the ketone. The concentration of the hydrogen iodide is, however, so small, even when the reaction is completed, that the quantity of iodine thus liberated is not such as to prevent the determination of the rate of tautomeric change. There can be little doubt, however, that the subsequent liberation of iodine from the hydrogen iodide formed during the reaction is responsible for the slight decrease in the reaction velocity which was observed in certain cases towards the end of the period of observation.

For a given concentration of the acid catalyst the rate of change is proportional to the concentration of the ketone, and table I gives a summary of the velocities of tautomeric change (k) referred to a ketone concentration of one mol. per litre and 0·1 molar sulphuric acid as catalyst. In the majority of the experiments the actual concentration of the ketone varied from 0·12 to 0·18 mol. per litre, and the added iodine corresponded with an original concentration of about 0·01 mol. per litre. To permit of a direct comparison of the rates of enolisation of closely related ketones, some of the data obtained in the previous series of measurements have been expressed in terms of unit ketone concentration and incorporated in the table.

TABLE I.

	$k \times 10^6$.		$k \times 10^6$.
Dimethyl ketone	288	Methyl butyl ketone	318
Diethyl ketone	236	Methyl *iso*butyl ketone	247
Dipropyl ketone	202	Methyl *tert.*-butyl ketone	132
Methyl propyl ketone	270	Methyl hexyl ketone	306
Methyl *iso*propyl ketone	200	Acetophenone	108
		Benzyl methyl ketone	395
		Propiophenone	24

From the above data it is evident that the rate of tautomeric change of symmetrical aliphatic ketones diminishes as the number of carbon atoms in the alkyl group increases. The percentage decrease in the reactivity is approximately the same on passing from the dimethyl to the diethyl ketones as in the transition from the diethyl to the dipropyl compound. In contrast with this regularity it should be noted that the reactivities of the successive methyl alkyl ketones vary irregularly, as is evident from the series—dimethyl (288), methyl ethyl (300), methyl propyl (270), methyl butyl (318), methyl hexyl (306). It does not seem possible at present to offer any satisfactory explanation of the observed differences.

The influence of the constitution of the alkyl group in this series is, however, clearly defined, as is seen by a comparison of the two methyl propyl and the three methyl butyl ketones. Substitution of the normal by the *iso*alkyl group reduces the reactivity in each case by about 25 per cent., whilst the reactivity of the normal butyl ketone is about two and a-half times as great as that of the corresponding tertiary butyl compound. These changes in reactivity are in the direction anticipated, for the replacement of one of the two reactive hydrogen atoms in the normal alkyl group must lead to a diminution in the reactivity of the ketone if the alkyl group in question is directly concerned in the tautomeric change. In the case of methyl *tert.*-butyl ketone, the butyl group represents an inactive radicle, and the methyl group alone can be involved in the tautomeric change. Compared with dimethyl ketone, it may be noticed that the reactivity of methyl *tert.*-butyl ketone is approximately one half as large, a relationship which may serve to throw some light on the nature of the keto $\rightarrow$ enol transformation in the case of the dialkyl ketones. On the other hand, the reactivity of acetophenone, which also contains a non-reactive group, is considerably smaller than that of methyl *tert.*-butyl ketone, which shows that the tendency of the $CH_3\cdot CO\cdot$ group to undergo enolisation is appreciably diminished by the proximity of the negative phenyl group. It is evident, however, that the part played by the

phenyl group in its influence on the interaction between alkyl hydrogen and the ketonic group is of a somewhat complex character, for the rate of tautomeric change of benzyl methyl ketone is greater than that of any other ketone which has been investigated. In the expectation that dibenzyl ketone would exhibit a still greater rate of change, experiments were also made with this substance. This supposition was not confirmed, but since the rate of progress of the change, as measured by the fall in the iodine concentration, is not constant, it is probable that some other change is involved, and, in consequence, a quantitative comparison of this substance with other ketones is out of the question.

In table II are recorded the rates of tautomeric change of certain substituted acetophenones. These measurements were undertaken in order to ascertain the influence of substitution in the benzene nucleus on the enolisation tendency of the $CH_3 \cdot CO \cdot$ group. On account of the smaller solubility of these ketones in 40 per cent. alcohol, it was necessary to conduct the investigation of these in more dilute solution. The concentration of the ketone was about 0·025 molar, that of the iodine initially present about 0·004 molar, with 0·1 molar sulphuric acid as catalyst. Parallel experiments with and without potassium iodide gave practically identical results, and blank experiments, in which the catalysing acid was absent, showed only relatively small changes in the iodine titre during the time occupied by the observations with the acid catalyst, except in the case of *p*-aminoacetophenone. In the blank experiment with this, a quantity of sulphuric acid equivalent to the ketone present was added, and the rate of disappearance of iodine observed under these conditions was applied to the correction of the data obtained when the acid added was in excess of that of the ketone to the extent of 0·1 mol. per litre.

TABLE II.

Ketone.	$k \times 10^6$.
Acetophenone	108
p-Bromoacetophenone	90
p-Iodoacetophenone	(90) *
p-Aminoacetophenone sulphate	80
m-Nitroacetophenone	45
ω-Bromoacetophenone	0

According to these data, substitution of hydrogen in the phenyl group by bromine, iodine, the nitro-group, or the acidified amino-group leads to a reduction of the rate of tautomeric change. If

* On account of the small solubility of this substance it was examined in 60 per cent. alcoholic solution and found to change at the same rate as the corresponding bromo-compound.

the positive character of the amino-group is more than neutralised by the mineral acid, the effect of the substituent is in all cases to increase the negative character of the phenyl group, and this is doubtless the cause of the diminished rate of enolisation.

In the case of ω-bromoacetophenone, the change, if it occurs at all, takes place very slowly, and the substitution of a hydrogen atom of the methyl group by a negative atom or group would therefore appear to inhibit the tautomeric change.

Experimental.

In the appended tables some of the dynamic measurements are recorded, from which the relative reactivities of the ketones have been calculated. In these tables c represents the ketone concentration, x the observed iodine concentration at time t, x_0 the concentration at $t=0$, and x_t the concentration calculated from $x_t=x_0-k't$, in which k' is the constant rate of change. Concentrations are expressed in mols. per litre, time in minutes.

Dipropyl Ketone.

$c=0{\cdot}1532$; $k'=31{\cdot}0\times10^{-6}$.

t.	0.	30.	60.	90.	130.
$x.10^4$	90·7	81·4	72·4	62·8	50·9
$x_t.10^4$	(90·7)	81·4	72·1	62·8	50·4

Methyl iso*Propyl Ketone.*

$c=0{\cdot}185$; $k'=36{\cdot}5\times10^{-6}$.

t.	0.	20.	40.	70.	100.	130.
$x.10^4$	91·9	84·7	77·2	66·2	55·5	45·1
$x_t.10^4$	(91·9)	84·6	77·3	66·4	55·4	44·5

Methyl iso*Butyl Ketone.*

$c=0{\cdot}1512$; $k'=37{\cdot}3\times10^{-6}$.

t.	0.	30.	60.	90.	120.
$x.10^4$	101·3	90·1	79·0	68·2	58·2
$x_t.10^4$	(101·3)	90·1	78·9	67·7	56·6

Methyl tert.*-Butyl Ketone.*

$c=0{\cdot}1285$; $k'=17{\cdot}0\times10^{-6}$.

t.	0.	40.	100.	140.	180.	220.
$x.10^4$	88·6	81·2	71·2	64·8	58·4	51·9
$x_t.10^4$	(88·6)	81·8	71·6	64·8	58·0	51·2

Benzyl Methyl Ketone.

$c = 0\cdot121$; $k' = 48\cdot0 \times 10^{-6}$.

t.	0.	40.	60.	85.	105.
$x.10^4$	77·5	57·1	48·4	36·4	27·4
$x_t.10^4$	(77·5)	58·3	48·7	36·7	27·1

Acetophenone.

$c = 0\cdot0274$; $k' = 2\cdot95 \times 10^{-6}$.

t.	0.	150.	257.	347.	430.
$x.10^4$	38·8	34·5	31·3	28·6	26·0
$x_t.10^4$	(38·8)	34·4	31·2	28·6	26·1

p-*Bromoacetophenone.*

$c = 0\cdot0250$; $k' = 2\cdot2 \times 10^{-6}$.

t.	0.	120.	240.	360.
$x.10^4$	40·1	37·5	34·8	32·1
$x_t.10^4$	(40·1)	37·45	34·8	32·2

m-*Nitroacetophenone.*

$c = 0\cdot0251$; $k' = 1\cdot1 \times 10^{-6}$.

t.	0.	120.	240.	360.
$x.10^4$	40·0	38·7	37·4	36·1
$x_t.10^4$	(40·0)	38·7	37·35	36·05

p-*Aminoacetophenone Sulphate.*

$c = 0\cdot0247$; $k' = 1\cdot95 \times 10^{-6}$.

t.	0.	69.	230.	320.	443.
$x.10^4$	37·95	36·4	33·7	31·7	29·35*
$x_t.10^4$	(37·95)	36·6	33·45	31·7	29·3

Physical Chemistry Laboratory,
The University, Leeds.

* These numbers are corrected for the rate at which iodine was found to disappear in a parallel experiment without acid catalyst.

CXCVI.—*The Formation of Glyoxalines from Acyl Derivatives of α-Keto-β-anilino-αβ-diphenylethane.*

By Arthur Ernest Everest (Priestley Research Scholar of the University of Birmingham) and Hamilton McCombie.

In the course of some work in these laboratories on the action of heat on a mixture of benzaldehydecyanohydrin and aniline, a compound was isolated, which, on analysis, was found to have the empirical formula $C_{27}H_{20}N_2$. This substance was found to be basic, readily yielding well-characterised, stable salts, and it could be distilled without decomposition. It was suspected that this compound was 1:2:4:5-tetraphenylglyoxaline (I), and, as α-keto-β-anilino-αβ-diphenylethane (II) was also one of the products isolated in this reaction, an attempt was made to synthesise the tetraphenylglyoxaline with α-keto-β-anilino-αβ-diphenylethane as the starting point. This synthesis proved successful:

$$\left.\begin{matrix}\mathrm{CPh\cdot NPh} \\ \| \\ \mathrm{CPh{-}{-}{-}N}\end{matrix}\right>\mathrm{CPh} \qquad \mathrm{COPh\cdot CHPh\cdot NHPh} \qquad \mathrm{COPh\cdot CHPh\cdot NPhBz}$$

(I.) (II.) (III.)

The first step in the synthesis consisted in the conversion of α-keto-β-anilino-αβ-diphenylethane into α-keto-β-benzoylanilino-αβ-diphenylethane (III). This benzoyl derivative was then heated in a sealed tube with aqueous ammonia, and the tetraphenylglyoxaline thus obtained.

An attempt was next made to bring about a similar condensation to glyoxalines employing other acyl derivatives of α-keto-β-anilino-αβ-diphenylethane. The acetyl derivative (IV), when heated in a sealed tube with aqueous ammonia, was found to yield 1:4:5-triphenyl-2-methylglyoxaline (V):

$$\mathrm{COPh\cdot CHPh\cdot NPhAc} \qquad \left.\begin{matrix}\mathrm{CPh\cdot NPh} \\ \| \\ \mathrm{CPh{-}{-}{-}N}\end{matrix}\right>\mathrm{CMe} \qquad \mathrm{COPh\cdot CHPh\cdot NPh\cdot CHO}$$

(IV.) (V.) (VI.)

In a similar manner, the formyl derivative of α-keto-β-anilino-αβ-diphenylethane (VI) yielded 1:4:5-triphenylglyoxaline (VII):

$$\left.\begin{matrix}\mathrm{CPh\cdot NPh} \\ \| \\ \mathrm{CPh{-}{-}{-}N}\end{matrix}\right>\mathrm{CH.}$$

(VII.)

This method for the preparation of glyoxalines is similar to Ladenburg's method for the formation of benziminazoles (*Ber.*, 1875, **8**, 677; 1878, **11**, 826) by the condensation of *o*-phenylene-

diamines with an acid chloride or anhydride; acyl compounds of the phenylenediamine are formed as intermediate products, thus:

$$C_6H_4{<}{NH_2 \atop NH_2} \longrightarrow C_6H_4{<}{NH \diagdown \atop NH_2}COR \longrightarrow C_6H_4{<}{NH \atop -N}{\gg}CR.$$

Another series of somewhat similar reactions has been described by Meldola and Hay (Trans., 1908, **93**, 1695; 1909, **95**, 1033), where these investigators describe the formation of benziminazoles by the interaction of 2:3:5-trinitro-4-acetylaminophenol with primary amines.

By means of the reaction which we describe in this communication, we are furnished with a ready means of obtaining glyoxalines with substituents attached to the nitrogen atom. Previously, such substituted glyoxalines could be obtained by two methods, neither of which is very convenient.

(1) By treating the silver salt of the glyoxaline with an alkyl iodide. This method has the great disadvantage that the substituent introduced must be an aliphatic radicle.

(2) By oxidation of the mercaptans of the glyoxalines which are obtained from the thiocarbamides (*Ber.*, 1889, **22**, 1353; 1892, **25**, 2354; 1893, **26**, 2204).

This reaction consists in closing up a chain of four atoms to a ring consisting of five atoms, and thus gives us a closer insight than has been previously possible into the actual mechanism of the ordinary glyoxaline formation from α-diketones, ammonia, and an aldehyde.

In the formation of these three glyoxalines by heating together the acyl derivatives of α-keto-β-anilino-$\alpha\beta$-diphenylethane with ammonia, there was obtained, in varying quantities, a second substance, which analyses showed to have the composition $C_{28}H_{20}N_2$. This substance is 2:3:5:6-tetraphenylpyrazine (VIII):

$$\begin{array}{l} CPh\cdot N\cdot CPh \\ \| \qquad\quad \| \\ CPh\cdot N\cdot CPh \end{array}$$

(VIII.)

2:3:5:6-Tetraphenylpyrazine has been obtained in different ways by several investigators. Bülow (*Ber.*, 1893, **26**, 1973) prepared it by boiling together benzaldehyde and formamide for two hours. It has also been obtained by J. Erdmann (*Annalen*, 1865, **135**, 55), Japp and Wilson (Trans., 1886, **49**, 826), and Leucart (*J. pr. Chem.*, 1890, [ii], **41**, 333) by heating benzoin with alcoholic ammonia. It is doubtless by means of the latter reaction that the substance is formed in the present case, hydrolysis of the acyl-α-keto-β-anilino-$\alpha\beta$-diphenylethane to benzoin preceding that reaction.

Some interesting and characteristic colour changes are noticeable

in dealing with α-keto-β-anilino-αβ-diphenylethane and its acyl derivatives in acid and in alkaline solutions.

α-Keto-β-anilino-αβ-diphenylethane itself is yellow, and gives rise to yellow solutions, but these solutions become colourless on the addition of acids, whilst the yellow colour is restored on the addition of alkali. The acyl derivatives are all white solids giving colourless solutions, but these solutions become deep yellow on the addition of a drop of alkali, and the colour is destroyed by the addition of acid. These colour changes seem to indicate the existence of each of these substances in two modifications; most probably these two are the ketonic and the enolic modifications. Thus, for the benzoyl derivative itself, the free substance most probably has the ketonic structure represented by the formula IX, whilst in the presence of alkali it has the enolic structure represented by the formula X. It is hoped to investigate this change more fully at a later date:

COPh·CHPh·NPhBz	HO·CPh:CPh·NPhBz
(IX.)	(X.)

Experimental.

α-*Keto-β-benzoylanilino-αβ-diphenylethane* (III, p. 1746).

This substance was prepared from α-keto-β-anilino-αβ-diphenylethane by the Schotten-Baumann reaction. When crystallised from methylated spirit or methyl alcohol, it separates in shining, colourless plates or leaflets, melting at 149°. Its alcoholic solution gives a yellow coloration on the addition of alkali, but this coloration is destroyed by neutralising the solution with acid:

0·2196 gave 0·6676 CO_2 and 0·1084 H_2O. C = 82·91; H = 5·48.
$C_{27}H_{21}O_2N$ requires C = 82·87; H = 5·37 per cent.

1:2:4:5-*Tetraphenylglyoxaline*, $C_{27}H_{20}N_2$ (I, p. 1746).

This substance was obtained by heating equal parts by weight of concentrated aqueous ammonia (D 0·880) and the above compound in a sealed tube to 210—220° for seven or eight hours. The product, a sticky, yellow, crystalline mass, was washed free from resins with a small quantity of ether, then crystallised from methylated spirit. A yield of about 70—80 per cent. was obtained.

1:2:4:5-*Tetraphenylglyoxaline* separates from alcohol in long, colourless needles, melting at 215°. It is readily soluble in glacial acetic acid, aniline, or benzene, fairly so in hot absolute alcohol, methyl alcohol, acetone, or light petroleum, but less so in the cold solvents, and crystallises well from any of them; it is very sparingly

soluble in ether, and is insoluble in water. It is stable towards alkalis, and can be distilled unchanged:

0·1819 gave 0·5793 CO_2 and 0·0917 H_2O. C=87·06; H=5·60.
0·1884 „ 12·70 c.c. N_2 at 20° and 730·2 mm. N=7·54.
M.W. (by platinum salt)=376·5, 366·0, 374·5.
$C_{27}H_{20}N_2$ requires C=87·10; H=5·38; N=7·53 per cent.
M.W.=372.

In addition to the above-described glyoxaline, a substance, crystallising in fine, needle-shaped crystals, and melting at 243°, was always encountered when crystallising the crude product for the first time. This substance remained as an almost totally insoluble residue when the glyoxaline was dissolved in boiling methylated spirit. The quantity of this substance formed was small, only constituting about 1—2 per cent. of the weight of the glyoxaline. It was recrystallised from amyl alcohol, and proved to be 2:3:5:6-tetraphenylpyrazine (VIII). There separated also from the mother liquors from which the glyoxaline had been recrystallised, a very small quantity of a substance melting at 193—195°; sufficient of this substance for further examination was not obtained.

1:2:4:5-*Tetraphenylglyoxaline picrate*, $C_{27}H_{20}N_2,C_6H_3O_7N_3$, was prepared by adding a concentrated solution of picric acid in glacial acetic acid to a solution of the glyoxaline in the same solvent at about 100°. The colour deepened very considerably on mixing, and, on cooling, golden-yellow, shining leaflets separated. The picrate may be recrystallised from glacial acetic acid, or, better, from methylated spirit. It melts at 199°:

0·2510 gave 0·6039 CO_2 and 0·0910 H_2O. C=65·62; H=3·99.
$C_{33}H_{23}O_7N_5$ requires C=65·89; H=3·83 per cent.

The *hydrochloride*, after recrystallisation from glacial acetic acid, separates in large, transparent cubes, melting at 250°.

The *platinichloride* forms a salmon-pink, microscopically crystalline precipitate:

0·4045 gave 0·0680 Pt. Pt=16·81.
$(C_{27}H_{20}N_2)_2,H_2PtCl_6$ requires Pt=16·88 per cent.

α-Keto-β-acetylanilino-αβ-diphenylethane (IV, p. 1746).

This compound was prepared by Voigt (*J. pr. Chem.*, 1886, [ii], **34**, 9), but the method described by this investigator, using acetic anhydride alone, did not give a very satisfactory product, so that it was modified to the following: 17 grams of the base, 15 grams of acetic anhydride, and 2 grams of acetyl chloride were heated for a few minutes on a water-bath, and the product was poured

into cold water. The reaction was found to proceed smoothly only when some acetyl chloride was used in addition to the acetic anhydride. The product crystallised from ethyl or methyl alcohol in slender, colourless, glistening scales (or leaflets), melting at 153°.

This substance, like the benzoyl derivative, gave a deep yellow coloration when potassium hydroxide was added to an alcoholic solution; this colour disappeared with excess of acid.

1:4:5-*Triphenyl-2-methylglyoxaline*, $C_{22}H_{18}N_2$ (V, p. 1746).

This compound was prepared by heating equal parts by weight of aqueous ammonia (D 0·880) and the substance just described in a sealed tube to 200—230° for six to eight hours. On cooling, the product, which resembled that from the benzoyl derivative, was washed with a small quantity of ether, and recrystallised from methyl alcohol, when the glyoxaline separated in fairly large, colourless crystals, melting at 194°. The yield was 70—90 per cent. of the theoretical. A small quantity of tetraphenylpyrazine was also obtained:

0·2196 gave 0·6841 CO_2 and 0·1172 H_2O. C=84·93; H=6·07.
0·1778 ,, 13·40 c.c. N_2 at 9·0° and 743·9 mm. N=8·93.
$C_{22}H_{18}N_2$ requires C=85·16; H=5·81; N=9·03 per cent.

The *picrate* crystallises from methylated spirit in golden-yellow needles, melting at 180°:

0·2011 gave 0·4577 CO_2 and 0·0724 H_2O. C=62·11; H=4·02.
$C_{22}H_{18}N_2,C_6H_3O_7N_3$ requires C=62·34; H=3·90 per cent.

The *hydrochloride* separates from amyl alcohol in small, colourless crystals, melting sharply at 300°, with decomposition and evolution of gas.

The *platinichloride* was obtained as a salmon-pink, crystalline powder. It was best prepared from cold solutions, as the product was prone to accumulate in great masses if the reaction was carried out in hot solutions:

0·4420 gave 0·0830 Pt. Pt=18·78.
$(C_{22}H_{18}N_2)_2,H_2PtCl_6$ requires Pt=18·93 per cent.

α-Keto-β-formylanilino-αβ-diphenylethane (VI, p. 1746).

This substance was prepared by heating a mixture of two parts of the pure base with one part of anhydrous formic acid under reflux for about an hour. The resulting mixture was poured into cold water, when a semi-solid paste was obtained. Most of the excess of acid was then neutralised by sodium carbonate, after which the paste was sufficiently firm to allow of pouring off the water. After this had been done, the paste was dissolved in more than enough methylated spirit to keep all in solution in the cold,

and the excess of formic acid that still remained was neutralised by adding potassium hydroxide drop by drop until the colour of the solution turned to a deep yellow; after this process had been completed the whole of the product should still be in solution.

The alcoholic solution was then allowed to evaporate slowly in the cold, when the formyl derivative separated in colourless scales. The product thus obtained was recrystallised many times from methyl alcohol, and finally separated in small, colourless crystals, melting at 105°. This derivative was very soluble in most solvents. Like the benzoyl and acetyl derivatives it gave a deep yellow coloration with potassium hydroxide, which was destroyed on neutralising the solution with acid:

0·2511 gave 0·7338 CO_2 and 0·1251 H_2O. C=79·70; H=5·54.

$C_{21}H_{19}O_2N$ requires C=80·00; H=5·40 per cent.

1:4:5-*Triphenylglyoxaline*, $C_{21}H_{16}N_2$ (VII, p. 1746).

This substance was prepared by heating together in a sealed tube for six to eight hours at 210—220° equal quantities by weight of the formyl derivative just described and aqueous ammonia. The product resembled that obtained in the other cases, and was treated in the same manner. The glyoxaline was finally recrystallised from a mixture of three parts of methyl alcohol to two parts of water (by volume); from this mixture it separated in fine, silky needles, melting at 172°. The crystals were colourless, and very soluble in most solvents. The glyoxaline could be distilled unchanged. A small quantity of tetraphenylpyrazine was also formed:

0·1547 gave 0·4810 CO_2 and 0·0781 H_2O. C=84·80; H=5·61.

$C_{21}H_{16}N_2$ requires C=85·14; H=5·41 per cent.

The *picrate* crystallises from methyl alcohol in golden-yellow, needle-shaped crystals, melting at 215°:

0·1743 gave 0·3871 CO_2 and 0·0603 H_2O. C=62·13; H=3·84.

$C_{21}H_{16}N_2{\cdot}C_6H_3N_3O_7$ requires C=61·72; H=3·62 per cent.

The *hydrochloride*, as it proved to be very soluble in most solvents, was not isolated, but the *platinichloride* was prepared, and crystallised from dilute acetic acid:

0·0914 gave 0·0178 Pt. Pt=19·47.

$(C_{21}H_{16}N_2)_2,H_2PtCl_6$ requires Pt=19·46 per cent.

It is intended to extend this method to the synthesis of other glyoxalines and similar compounds.

THE UNIVERSITY,
EDGBASTON, BIRMINGHAM.

CXCVII.—*The Effect of Heat on a Mixture of Benzaldehydecyanohydrin and Aniline.*

By ARTHUR ERNEST EVEREST (Priestley Research Scholar of the University of Birmingham) and HAMILTON McCOMBIE.

SOME years ago, in the course of some work in these laboratories, it was observed that if benzylideneaniline and benzaldehydecyanohydrin are heated together for forty-eight to ninety-six hours, a white, crystalline substance with an exceptionally high melting point (above 350°) separated out from the boiling liquid. As the reaction took a long time to reach completion, it was probable that the benzylideneaniline was decomposed into its generators. Accordingly, a study was made of the products formed by the action of heat on a mixture of aniline and benzaldehydecyanohydrin.

When molecular proportions of these substances are heated together to 150°, before the end of half an hour a considerable amount of water is formed, and after that period the quantity of water does not increase. On cooling the product at this stage, anilinophenylacetonitrile may be isolated.

On heating the mixture of aniline and cyanohydrin for forty-eight to ninety-six hours, the following products were obtained:

(1) Dibenzoyldianilinostilbene, NPhBz·CPh⁚CPh·NPhBz.

(2) 1:2:4:5-Tetraphenylglyoxaline (Everest and McCombie, this vol., p. 1748).

(3) α-Keto-β-anilino-$\alpha\beta$-diphenylethane.

(4) Benzanilide.

In the formation of compound (1) oxidation by the atmospheric oxygen must be assumed, and hydrocyanic acid is evolved. The reaction may be represented by the following equation:

$$4C_6H_5\cdot CH(OH)\cdot CN + 2C_6H_5\cdot NH_2 + O_2 = C_{40}H_{30}O_2N_2 + 4HCN + 4H_2O.$$

The formation of substance (2) must be due to the action of ammonia (formed by the hydrolysis of the hydrocyanic acid) on the benzoyl derivative of α-keto-β-anilino-$\alpha\beta$-diphenylethane:

$$COPh\cdot CHPh\cdot NPhBz + NH_3 \longrightarrow \begin{matrix} CPh\cdot NPh \\ \| \\ CPh\text{---}H \end{matrix} \!\!>\! CPh.$$

The formation of compound (3) in this reaction may be explained in three ways. The benzaldehyde may condense to benzoin, and this may undergo further condensation with aniline, or hydrocyanic acid may be eliminated from the cyanohydrin and phenylanilinoacetonitrile, thus:

$$HO\cdot CHPh⁚NHPh + HO\cdot CPh\cdot CN = COPh\cdot CHPh\cdot NHPh + HCN.$$

The third alternative is that benzaldehyde and benzylideneaniline might condense together, thus:

$$\mathrm{Ph{\cdot}CHO + CHPh{:}NPh = COPh{\cdot}CHPh{\cdot}NHPh.}$$

The last method of formation is similar to the preparation of α-keto-β-*p*-toluidino-αβ-diphenylethane from benzylidene-*p*-toluidine and benzaldehyde by the action of potassium cyanide (*Ber.*, 1896, **29**, 1736).

The constitution of dibenzoyldianilinostilbene is established as follows: the analytical figures are in agreement with the formula $C_{40}H_{30}O_2N_2$, and it can be decomposed quantitatively by potassium hydroxide according to the following equation:

$$C_{40}H_{30}O_2N_2 + KOH = C_{33}H_{26}ON_2 + Ph{\cdot}CO_2K.$$

The substance formed in this reaction is benzoyldianilinostilbene, and its constitution is shown by its decompositions, which take place in two ways:

(*a*) by spontaneous oxidation of its solutions when exposed to the air;

(*b*) by heating the substance to 120—140°.

In the former case, solutions of the substance in several solvents underwent decomposition into benzanilide and dibenzoylaniline:

$$C_{33}H_{26}ON_2 + O_2 = C_{13}H_{11}ON + C_{20}H_{15}O_2N.$$

In the latter case, heat decomposed the substance, so that dibenzoyldianilinostilbene was regenerated, and benzanilide and benzildianil were produced.

The decompositions of benzoyldianilinostilbene are readily explained by the following equations:

$$(a)\quad \begin{array}{l}\mathrm{CPh{\cdot}NPhBz}\\ \|\\ \mathrm{CPh{\cdot}NHPh}\end{array} + O_2 \longrightarrow \mathrm{COPh{\cdot}NPhBz + COPh{\cdot}NHPh}$$

$$(b)\quad \left.\begin{array}{l}\mathrm{CPh{\cdot}NPhBz}\\ \|\\ \mathrm{CPh{\cdot}NHPh}\\ \\ \mathrm{CPh{\cdot}NHPh}\\ \|\\ \mathrm{CPh{\cdot}NPhBz}\end{array}\right\} \longrightarrow \begin{array}{l}\mathrm{CPh{\cdot}NPhBz}\\ \|\\ \mathrm{CPh{\cdot}NPhBz}\end{array} + \underset{\text{(I.)}}{\begin{array}{l}\mathrm{CPh{\cdot}NHPh}\\ \|\\ \mathrm{CPh{\cdot}NHPh}\end{array}}$$

Dianilinostilbene (I), which one would expect to be formed in this reaction, is oxidised by the oxygen of the air, forming benzanilide, or it may undergo a simultaneous rearrangement and oxidation, resulting in the production of benzildianil, $\mathrm{NPh{:}CPh{\cdot}CPh{:}NPh}$. Both these products have been identified in the reaction mixture.

If these conclusions be correct, then it should not be a matter of great difficulty to synthesise dibenzoyldianilinostilbene in such a way that its constitution would be obvious. A successful attempt was made by taking advantage of the above-mentioned decomposi-

tion by heat of monobenzoyldianilinostilbene. α-Keto-β-anilino-αβ-diphenylethane (II) was used as the starting point, and this was converted into the benzoyl derivative (III), which was then heated with aniline in the presence of potassium cyanide, when dibenzoyldianilinostilbene was obtained:

$$\begin{array}{ccc} \begin{array}{l} \mathrm{CHPh{\cdot}NHPh} \\ | \\ \mathrm{COPh} \end{array} & \begin{array}{l} \mathrm{CHPh{\cdot}NPhBz} \\ | \\ \mathrm{COPh} \end{array} & \begin{array}{l} \mathrm{CPh{\cdot}NPhBz} \\ \| \\ \mathrm{CPh{\cdot}NPhBz} \end{array} \\ \text{(II.)} & \text{(III.)} & \text{(IV.)} \end{array}$$

The occurrence of α-keto-β-anilino-αβ-diphenylethane and benzanilide in the tars formed in the reaction under investigation is in keeping with the above conclusions, and the course of the original reaction may, in all probability, be represented thus: benzaldehyde, in presence of hydrocyanic acid, undergoes condensation to benzoin, and this combining with the aniline present gives rise to the production of α-keto-β-anilino-αβ-diphenylethane. The next step consists in the benzoylation of the latter compound by the benzaldehyde in the presence of the atmospheric air, and then the benzoyl derivative thus produced condenses with aniline to yield monobenzoyldianilinostilbene, which is then decomposed, with the production of dibenzoyldianilinostilbene.

The reason that only one benzoyl group is eliminated by potassium hydroxide from dibenzoyldianilinostilbene may be that ring formation takes place. One benzoyl group might be eliminated from dibenzoyldianilinostilbene and a cyclic compound formed, thus:

$$\begin{array}{l} \mathrm{CPh{\cdot}NPhBz} \\ \| \\ \mathrm{CPh{\cdot}NPhBz} \end{array} \longrightarrow \begin{array}{l} \mathrm{CPh{\cdot}NPhBz} \\ \| \\ \mathrm{CPh{\cdot}NHPh} \end{array} \longrightarrow \begin{array}{l} \mathrm{CPh{\cdot}NPh} \\ \| \\ \mathrm{CPh{\cdot}NPh} \end{array}\!\!>\mathrm{CPh{\cdot}OH};$$

or, again, it is possible that the substance of high melting point may itself be a cyclic compound:

$$\begin{array}{l} \mathrm{CPh{\cdot}NPh} \\ \| \\ \mathrm{CPh{\cdot}NPh} \end{array}\!\!>\mathrm{CPh{\cdot}CO_2Ph}.$$

If, however, we assume these ring formulæ, we should have great difficulty in explaining the ready decompositions of the yellow base, both in solution and in the free state.

All attempts to obtain salts from dibenzoyldianilinostilbene resulted in the elimination of benzoic acid and the formation of the same salts as were obtainable from the monobenzoyl derivative. The only true derivative of the dibenzoyl compound which could be prepared was its compound with methyl iodide.

Benzoyldianilinostilbene yields a series of salts, of which the hydrochloride, platinichloride, and acetate were obtained. On attempting to prepare a picrate from either the dibenzoyl or the monobenzoyl compound, a substance was obtained which on analysis gave figures agreeing with a compound formed by the loss of a

molecule of water from one molecule of the monobenzoyl compound and one molecule of the picric acid. On heating with potassium hydroxide, this compound regenerated the base. Phenol itself and *o*- and *p*-nitrophenol yield compounds with benzoyldianilinostilbene, and it is proposed to investigate these compounds more fully later.

Experimental.

The reactions under investigation took place quite consistently, and with care, uniform yields of the two primary products (dibenzoyldianilinostilbene, $C_{40}H_{30}O_2N_2$, and 1:2:4:5-tetraphenylglyoxaline) were readily obtained.

The heating was carried out in conical Jena-glass flasks fitted with air condensers. The boiling mixture was generally seeded with a few crystals of dibenzoyldianilinostilbene.

The flasks containing the mixtures were heated in an air-bath kept at 150—160°. An air-bath was found most suitable for this purpose, because, in order to obtain the best results, the mixtures had to be kept just boiling. Whenever the mixture was, either, not kept boiling, or was allowed to boil too vigorously, excessive charring resulted, and the yield fell. It was found that the temperature requisite to secure slow boiling varied with the time, and that two exactly parallel experiments proceeded at different rates. By using an air-bath, and regulating the distance of the flasks from the bottom of the bath, it was possible to overcome these difficulties.

In the hope that the results obtained might lead to the elucidation of the changes taking place and to the determination of the substances that really take part in the reaction, a series of comparative experiments was made, employing different combinations of the materials; in each case the yield of dibenzoyldianilinostilbene was noted.

From the results of these experiments it was deduced that in order to obtain dibenzoyldianilinostilbene, both aniline and benzaldehydecyanohydrin must be present, and, further, that if these were present in molecular proportions, the yield was not so good as that obtained if two molecules of the cyanohydrin and one of the aniline were employed. Further, it was found that the yield obtained in the latter case was much the same as that resulting when aniline, benzaldehyde, and benzaldehydecyanohydrin, all in molecular proportions, were employed. Finally, no increase of yield was obtained by increasing the ratio of the cyanohydrin to aniline beyond the ratio of two to one. All these conclusions were verified by the later investigations, which have shown that in the dibenzoyldianilinostilbene molecule there exist two aldehyde residues for every aniline residue.

Experiments were also carried out on the action of continued heating on benzaldehydecyanohydrin and on phenylanilinoacetonitrile. In the former case great charring took place, and nothing but benzoic acid could be isolated. In the latter case a quantity of dibenzoyldianilinostilbene was obtained, and the tars remaining after the removal of this substance were further examined. By steam distillation there was obtained from them a quantity of an oil (which proved to be aniline), together with a smaller quantity of benzylideneaniline. This showed that the nitrile on heating underwent decomposition into hydrocyanic acid and benzylideneaniline. The latter substance was then hydrolysed; the aniline thus produced, not being required for the further reaction, remained behind, whilst the benzaldehyde formed entered into reaction to furnish the second aldehyde residue, shown by the other experiments to be at least advantageous, if not absolutely necessary, for the production of dibenzoyldianilinostilbene.

Dibenzoyldianilinostilbene, $C_{40}H_{30}O_2N_2$.

Although this was originally obtained by the prolonged action of heat on a mixture of benzylideneaniline (1 mol.) and benzaldehydecyanohydrin (2 mols.), it was found that the best method of preparation consisted in heating together aniline (1 mol.) with benzaldehydecyanohydrin (2 mols.). If these two substances were employed in molecular proportions, and one molecular part of benzaldehyde was added, almost as good a yield was obtained, but the isolation of the other products of the reaction was complicated by the excess of benzaldehyde remaining at the end of the reaction.

If aniline and benzaldehydecyanohydrin are heated together for half an hour at 150—160°, a quantitative yield of phenylanilinoacetonitrile can be obtained, but the heating was generally continued without the isolation of this compound. No apparent change occurred after the elimination of water required by this reaction until towards the close of the second day's heating (forty-eight hours), when the quiet boiling changed to a crackling. Soon after this change was observed, crystals began to separate from the boiling liquid, and continued to do so until the whole was interlaced to form a semi-solid mass. The yield generally reached its maximum in twenty-four to thirty hours after the separation of the crystals began, and was 25—40 per cent. of the theoretical.

The time requisite for the reaction was found to vary considerably. In some cases one hundred and twenty hours' heating was requisite to obtain a good yield, whilst occasionally an equally good yield was obtained after only forty-eight hours' heating. Many

experiments were carried out with the object of observing some connexion between the length of heating and the yield obtained, but they proved unsuccessful. Considerable experience is requisite in order to obtain good yields without charring and in reasonable time, but when this has been acquired, regular, good, and clean yields are readily obtained. During the early part of the heating a considerable quantity of hydrocyanic acid was liberated.

To separate the substance from the adhering tars, the contents of the flasks were either (*a*) mixed while warm with sufficient pure ether to produce a mobile liquid, and the crystals were collected and washed, or (*b*) allowed to remain overnight with ether equal in volume to three times that of the tars; after keeping, the substance was deposited as a crystalline mass, which was collected and washed. The tars obtained in these processes were kept for further treatment (p. 1762).

The crude dibenzoyldianilinostilbene obtained by this method was usually mixed with some tetraphenylglyoxaline; the quantity of glyoxaline was found to increase with the time of heating requisite in the preparation.

The dibenzoyldianilinostilbene was present in well-formed crystals, often of some considerable size, in which case they were found to be hard and brittle. Its complete separation was achieved by extracting the mixture in a Soxhlet apparatus with dry ether (free from alcohol); dibenzoyldianilinostilbene was insoluble, whilst tetraphenylglyoxaline was sparingly soluble in that solvent. To ensure a pure product all the lumps were crushed before extraction and occasionally during the process. The glyoxaline, if present to any considerable extent, separated in hard, granular crystals from the ether.

Dibenzoyldianilinostilbene, after purification by this means, was recrystallised from amyl alcohol, from which it separated in colourless, glistening, needle-shaped crystals, having a melting point well above 350°. It was fairly readily soluble in ethyl alcohol, methyl alcohol, or chloroform, very soluble in glacial acetic acid (in which solution, however, it was found to undergo decomposition), very sparingly so in acetone, and insoluble in ether or benzene. It does not crystallise well from solvents of low boiling point.

At first it was thought that this substance yielded a series of well-defined salts, but further investigation showed them to be salts of the decomposition product, monobenzoyldianilinostilbene, $C_{33}H_{26}ON_2$. By the action of acids or of alkalis, dibenzoyldianilinostilbene was found to undergo decomposition:

0·3020 gave 0·9295 CO_2 and 0·1500 H_2O. C = 83·94; H = 5·52.
0·3015 „ 0·9300 CO_2 „ 0·1505 H_2O. C = 84·12; H = 5·55.

0·2935 gave 12·95 c.c. N_2 (moist) at 19·5° and 734 mm. N=4·98.
0·3000 „ 13·40 c.c. N_2 „ „ 16·5° „ 738·5 mm. N=5·12.
$C_{40}H_{30}O_2N_2$ requires C=84·21; H=5·26; N=4·91 per cent.

Dibenzoyldianilinostilbene was also prepared by heating together the benzoyl derivative of α-keto-β-anilino-αβ-diphenylethane (1 mol.), aniline (1 mol.), and potassium cyanide (½ mol.). After eighteen hours' heating, the substance separated, and was treated as described in the other method of preparation. From the tars in this preparation, benzanilide was obtained, but no trace could be obtained of benzildianil.

Dibenzoyldianilinostilbene methiodide, $C_{40}H_{30}O_2N_2$,MeI, was prepared by adding a 50 per cent. solution of methyl iodide in absolute alcohol, drop by drop, to a solution of the dibenzoyl compound also in absolute alcohol. The methiodide was precipitated as a colourless, crystalline powder. It was insoluble in all ordinary organic solvents, and did not melt below 350°. If heated above that temperature, it charred and emitted fumes.

For analysis, the substance was prepared from a pure specimen of the dibenzoyl compound, and the resulting product was extracted twice with boiling absolute alcohol:

0·2623 gave 0·0863 AgI. I=17·78.
$C_{41}H_{33}O_2N_2I$ requires I=17·84 per cent.

Monobenzoyldianilinostilbene, $C_{33}H_{26}ON_2$.

Dibenzoyldianilinostilbene, when treated with acids, gave what were at first supposed to be true salts, but analysis proved that this was not the case. Further, on treating these salts with alkali, the original substance was not regenerated, but a yellow solid was obtained. This yellow solid could also be obtained by boiling dibenzoyldianilinostilbene with *N*/2-aqueous potassium hydroxide with the addition of a few drops of alcohol. It was found to be the true base corresponding with the above-mentioned salts. It was unstable in all solvents except alcohol, and in that solvent it was so sparingly soluble that recrystallisation was impossible. The yellow base was prepared for analysis by dissolving the pure dibenzoyldianilinostilbene in alcohol, adding *N*/2-aqueous potassium hydroxide drop by drop until a precipitate just began to form, and cooling the mixture, when the product separated in small, glistening crystals, melting at 212°, which were ground, boiled with water, and then washed with alcohol and ether:

0·2347 gave 0·7283 CO_2 and 0·1201 H_2O. C=84·63; H=5·69.
0·1799 „ 9·50 c.c. N_2 (moist) at 15° and 729·5 mm. N=5·91.
$C_{33}H_{26}ON_2$ requires C=84·98; H=5·58; N=6·01 per cent.

The fact that a benzoyl group had been eliminated in this reaction was shown by the precipitation of benzoic acid on acidification of the filtrate from the monobenzoyl compound. In order that this decomposition might be caused to yield an estimate of the molecular weight of the original dibenzoyl compound, the reaction was carried out quantitatively.

Three to four grams of the substance were heated under reflux with 25 c.c. of *N*-aqueous potassium hydroxide in the presence of a little alcohol. The product was collected, washed, and weighed. The excess of alkali was estimated in the filtrate:

3·556 gave 0·765 benzoic acid and 2·82 base.

The equation $C_{40}H_{30}O_2N_2 + KOH = C_{33}H_{26}ON_2 + C_7H_5O_2K$ requires 0·762 benzoic acid and 2·90 base.

A colourless modification of monobenzoyldianilinostilbene was obtained in an attempt to recrystallise the yellow variety from alcohol by spontaneous evaporation of the solvent; it crystallised in feathery, colourless crystals. This product, on heating, was found to change into the yellow form at about 160—180°, and then melted at 212°. It gave the same salts as the yellow modification.

Benzoyldianilinostilbene hydrochloride crystallised from acetic acid or from alcohol in colourless crystals, melting above 350°. When heated on platinum foil, the substance melted with decomposition and evolution of gas. The base could be regenerated by warming with potassium hydroxide or carbonate:

0·2326 gave 0·0866 AgCl. Cl = 9·21.

$(C_{33}H_{26}ON_2)_3,4HCl$ requires Cl = 9·20 per cent.

The *platinichloride*, prepared in the usual way, was washed with glacial acetic acid and water, and dried:

0·4125 gave 0·0727 Pt. Pt = 17·62.

$(C_{33}H_{26}ON_2)_3,4HCl,(PtCl_4)_2$ requires Pt = 17·58 per cent.

The *acetate*, $C_{33}H_{26}ON_2,2C_2H_4O_2$, was recrystallised from water, and formed colourless, needle-shaped crystals, melting at 335°:

0·2205 gave 0·6110 CO_2 and 0·1210 H_2O. C = 75·74; H = 6·11.

$C_{37}H_{34}O_5N_2$ requires C = 75·77; H = 5·80 per cent.

Compounds formed by Benzoyldianilinostilbene with Phenols.

Compound with Picric Acid, $C_{33}H_{25}ON_2 \cdot C_6H_2(NO_2)_3$.—This was prepared by adding a hot concentrated solution of picric acid in glacial acetic acid or alcohol to a solution of the benzoyl compound (or of the dibenzoyl compound) in the same solvent. The product was recrystallised from methyl or ethyl alcohol, when it separated in slender, silky needles, melting at 274·5°.

When this substance was boiled with aqueous potassium

hydroxide in presence of a few drops of alcohol, the base was regenerated. Potassium carbonate, however, did not bring about this decomposition.

Analyses showed that this substance was not a true picrate, but was a compound resulting by the elimination of a molecule of water from one molecule of the base and one of picric acid:

0·2003 gave 0·5066 CO_2 and 0·0715 H_2O. C=68·98; H=3·98.
0·2000 „ 18·40 c.c. N_2 (moist) at 19° and 722·9 mm. N=10·23.
$C_{39}H_{27}O_7N_5$ requires C=69·13; H=3·99; N=10·34 per cent.

Compound with o-*Nitrophenol*,
$C_{33}H_{25}ON_2{\cdot}C_6H_4{\cdot}NO_2,C_6H_4(NO_2){\cdot}OH$.
—This cannot be prepared in solution, but was readily obtained by heating together rapidly the two components until the whole mass became liquid and the vigorous evolution of water had ceased. The molten mass was poured into about twice its own volume of methylated spirit. It was recrystallised from a mixture of three parts of methyl alcohol and two parts of water, and separated in orange-yellow, hexagonal plates, melting at 183°, with the production of a deep red substance, which became solid and melted between 250° and 300°. This red compound could be obtained from the original substance by crystallisation from a mixture of chloroform and light petroleum, when it did not melt below 350°. On crystallising the red substance from methyl or ethyl alcohol, the orange-yellow compound was obtained.

Analysis of the substance recrystallised from alcohol gave:

0·2004 gave 0·5459 CO_2 and 0·0861 H_2O. C=74·29; H=4·77.
$C_{45}H_{34}O_6N_4$ requires C=74·38; H=4·68 per cent.

Compound with p-*Nitrophenol*,
$C_{33}H_{25}ON_2{\cdot}C_6H_4{\cdot}NO_2,C_6H_4(NO_2){\cdot}OH$.
—This was prepared in the same way as the *o*-nitrophenol compound, and was recrystallised from the same solvent, from which it was deposited in clusters of lemon-yellow, hexagonal plates, melting at 210—212°. This compound showed no change on melting:

0·2092 gave 0·5705 CO_2 and 0·0890 H_2O. C=74·38; H=4·73.
$C_{45}H_{34}O_6N_4$ requires C=74·38; H=4·68 per cent.

Compound with Phenol, $C_{33}H_{25}ON_2{\cdot}C_6H_5,2C_6H_5{\cdot}OH$.—This was prepared in the same way as the compounds with the nitrophenols, and was recrystallised, first from methylated spirit, and then from absolute alcohol, when it formed colourless crystals, melting at 226°:

0·2279 gave 0·6955 CO_2 and 0·1229 H_2O. C=83·24; H=5·99.
0·1932 „ 6·60 c.c. N_2 (moist) at 10·0° and 722·9 mm. N=3·92.
$C_{51}H_{41}O_3N_2$ requires C=83·84; H=5·75; N=3·84 per cent.

Decompositions of Benzoyldianilinostilbene.

Benzoyldianilinostilbene was found to be very unstable when in solution or when heated.

In Solution.—When the substance was dissolved in chloroform, light petroleum, benzene, amyl alcohol, or acetone, and allowed to remain exposed to the air at the ordinary temperature, the pale yellow solution first obtained gradually darkened; thus, in chloroform solution the colour was found to have darkened very appreciably in one hour, and even less if the solution was kept warm. At the end of a day or so the solution became deep brown, and, if the solution was concentrated, crystals separated, which, on recrystallisation, melted at 163°, and proved to be benzanilide.

From the filtrate, after the separation of the benzanilide, a second substance was isolated by concentrating the solution to a pasty mass, and then adding sufficient methylated spirit to dissolve the residue when boiled. After filtration and cooling, the solution deposited long, needle-shaped crystals, which, after recrystallisation, melted at 163°. This substance was proved to be dibenzoylaniline by analysis (Found, C = 79·14; H = 5·04; N = 4·67. Calc., C = 79·7; H = 4·98; N = 4·65 per cent.), and by a mixed melting-point determination. Hence in solution benzoyldianilinostilbene undergoes oxidation, yielding benzanilide and dibenzoylaniline. No other product could be isolated.

By Heat.—Benzoyldianilinostilbene, on being heated to 120—140° for a short time, was transformed into a jelly-like mass, which, on cooling, became quite brittle, and had a dirty yellowish-brown colour. On extracting the mass for a short time with benzene, some of it dissolved, and there remained a white, powdery residue, which did not melt below 350°, and proved to be dibenzoyldianilinostilbene. This was proved by the fact that with potassium hydroxide it yielded benzoic acid and monobenzoyldianilinostilbene. The benzene solution deposited crystals of benzanilide.

If instead of extracting the mass with benzene, ether was used, then from the filtrate a yellow substance separated, which, on recrystallisation from alcohol or ether, yielded well-formed crystals, melting at 145—147°. This substance was shown to be benzildianil by its ready hydrolysis with acids to benzil and aniline (Siegfeld, *Ber.*, 1892, **25**, 2601). Benzildianil was also obtained in small quantities by heating together α-keto-β-anilino-$\alpha\beta$-diphenylethane and aniline. Hence by the action of heat, benzoyldianilinostilbene yields dibenzoyldianilinostilbene, benzildianil, and benzanilide.

1:2:4:5-*Tetraphenylglyoxaline*, $C_{27}H_{20}N_2$.

As has been stated, crude dibenzoyldianilinostilbene is mixed with this glyoxaline, the identity of which has been established by synthesis (Everest and McCombie, *loc. cit.*).

When the tars from which dibenzoyldianilinostilbene had been obtained were further heated, another small quantity of this substance was produced, together with a considerable quantity of the glyoxaline; indeed, if the original reaction had been allowed to proceed to completion, the product on further heating was almost entirely the glyoxaline. The glyoxaline was separated from the residual tars by means of ether, and was thus obtained directly in a crystalline condition. It was recrystallised from methylated spirit, and melted at 215°. (Found, C=86·72; H=5·41; N=7·41. Calc., C=87·1; H=5·38; N=7·53 per cent.) The general properties of this substance have already been described by us (*loc. cit.*).

α-Keto-β-anilino-αβ-diphenylethane, $C_{20}H_{17}ON$.

This substance was isolated on several occasions, but not regularly, from the residual tars after the separation of dibenzoyldianilinostilbene. It was always obtained when that substance had separated earlier than usual, and when in such cases, the tars were allowed to remain, sometimes merely overnight, sometimes for several days. There seems every reason to believe that α-keto-β-anilino-αβ-diphenylethane is a regular constituent of the tars at this period of the reaction, and that its well known property of remaining in a supercooled condition accounts for its being isolated only occasionally.

The crystals were collected, washed with ether, and recrystallised from methylated spirit, when they melted at 98°. (Found, C=83·58; H=6·05; N=5·04. Calc., C=83·63; H=5·92; N=4·88 per cent.) The substance gave a hydrochloride melting at 200—202° (Lachowicz, *Monatsh.*, 1893, **14**, 280, gives 183°), an acetyl derivative melting at 153°, and with alcoholic potassium hydroxide it gave a purple-violet coloration. Finally, a mixed melting-point determination with a synthetic specimen proved them to be identical.

Benzanilide.

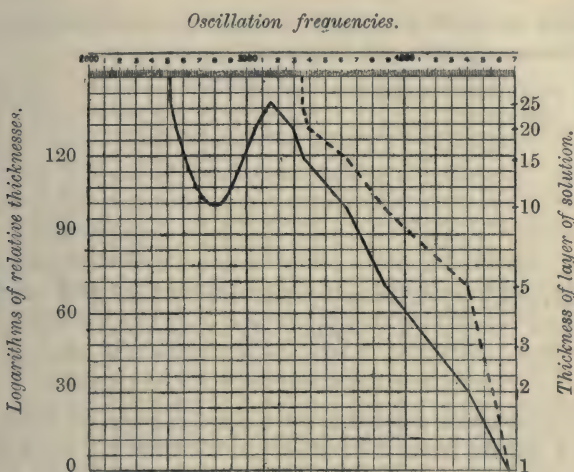
This was met with in the tars from the original reaction that had been kept for several weeks. A crystalline deposit was noticed, which, on recrystallisation, proved to be mainly tetraphenylglyoxaline, but after this had separated the mother liquors deposited

shining, plate-like crystals (m. p. 160°), which were shown to be benzanilide.

Absorption Spectra of Benzoyldianilinostilbene and of its Salts.

With the view of obtaining some insight into the relationships between the two forms of this base and its salts, a series of photographs was taken of the absorption spectra of these in solution. The solutions used were molecularly equivalent, and contained about 1 millimolecule per 12,500 c.c.

The two forms of the base showed very different absorptions, as shown in the diagram. The yellow variety showed a distinct band



Yellow variety of base in absolute alcohol ————
Colourless variety of base in absolute alcohol – – – –
both 1 *mg.-mol. in* 12,500 *c.c.*

near the visible end of the spectrum, together with general absorption in the regions more remote from the visible end. There was no fluorescence shown at the end of the tube during exposure.

The colourless variety, which was free from halogen, exhibited no band at all, but showed general absorption at the end of the spectrum furthest from the visible. Bright fluorescence was observed during exposure.

The hydrochloride showed identical absorption with that of the colourless variety of the base. It also showed the same bright fluorescence.

If a few drops of concentrated hydrochloric acid were added to the solution of the yellow variety, then the spectrum shown was that of the hydrochloride, and fluorescence was observed. If, on the

other hand, a few drops of aqueous potassium hydroxide were added to a solution of the colourless variety, the absorption spectrum showed that a considerable portion (but not all) of the base had been converted into the yellow variety. The band characteristic of the yellow form had become developed, but was not so distinct as in the case of the pure yellow form. Furthermore, the fluorescence, although greatly weakened, was still visible. This solution was not found to change on keeping.

From these results it appears evident that the salts which are colourless are the salts, not of the yellow base, but of its colourless modification.

We desire to thank Dr. C. K. Tinkler for his kind assistance in the spectroscopic portion of this work.

THE UNIVERSITY, EDGBASTON,
BIRMINGHAM.

CXCVIII.—*Composition of the Essential Oil of Myrica Gale, L.*

By SAMUEL SHROWDER PICKLES.

BOG MYRTLE or sweet gale (*Myrica Gale*, L.) is a well known shrub, varying in height from 2 to 5 feet, which occurs in marshy and moorland districts in Northern and Arctic Europe, Asia, and America. It is abundant in Scotland, northern England, and Ireland, and also occurs, although more rarely, in the south and east of England.

The plant contains a volatile oil, which has a characteristic odour. Mention is made of the "fragrant gale" or "bog myrtle" by several of the English classical writers, and in Scotland the sweet gale has long been the badge of the Campbells.

The shrub is known by various names in different countries. It is the "bay bush" of North America, and is also known as "willow myrtle" and Dutch myrtle.

The essential oil of *Myrica Gale* does not seem to have had any extensive application. The plant itself was formerly employed as a drug under the name "herba myrti brabanti," but is no longer used in medicine. Dr. J. Chevalier has recently found that the essential oil acts as a powerful purgative (*Bulletin*, Roure Bertrand Fils, April, 1910, p. 57). The bark of the plant is said to yield a

tannin, and the flower buds are stated to contain a yellow colouring matter (Engler and Prantl).

The oil appears to have been first examined by Rabenhorst in 1837 (Gildemeister and Hoffmann, *Volatile Oils*, p. 331), who found that, on distillation, the leaves of *M. Gale* yielded 0·65 per cent. of a brownish-yellow oil, having D 0·876. It is also stated that at 17·5° the oil congeals partly, and at 12·5° completely, to a crystalline mass, and that it contains 70 per cent. of camphor (?) (*loc. cit.*). A more recent examination has been made by Messrs. Roure Bertrand Fils (see *Bulletin*, April, 1910, p. 55), who determined the usual physical and chemical constants of the oil obtained from the branches.

There seems, however, to be no information on record regarding the chemical constituents of the oil, and so, having a small quantity of oil at his disposal, the author decided to identify, as far as possible, the component substances.

The bog myrtle from which the oil described in the present paper was derived was collected for Professor Dunstan in Argyllshire, N.B., and at his suggestion the author undertook the extraction and examination of the oil.

Two consignments of raw material have been examined, both of which were obtained from Argyllshire. The first consisted of about 30 lbs. of leaves and stems, and contained a rather large proportion of stems. The material had a slight herb-like odour somewhat suggestive of sage.

For the extraction of the oil the material was first cut up in a chaff-cutting machine, and then subjected to distillation in steam. The yield of oil from this consignment of the plant was found to be 0·076 per cent. The oil was pale yellow, had a characteristic, pleasant odour recalling that of sage, but somewhat more camphoraceous. On dilution with alcohol, or on remaining for some time in the cold, a solid material separates in colourless, shining, leafy crystals.

The second specimen, received at a later date, consisted of 42½ lbs. of bog myrtle, mainly leaves, the twigs being present to a small extent only. The leaves had the pleasant characteristic odour, and were partly dry. The yield of oil on distillation was 43 c.c., or 39·2 grams = 0·203 per cent.

The two oils thus obtained differed slightly in their physical and chemical characters, as will be seen from the following table. For comparison, the corresponding values obtained by Messrs. Roure Bertrand Fils for the oil from the branches of *M. Gale* are included.

	Oil from leaves and twigs.	Oil mainly from leaves.	Oil from branches. (Roure Bertrand Fils.)
Yield per cent.	0·076	0·203	0·045
Sp. gr. at 15°	0·915	0·912	at 25° = 0·8984
α_D (100 mm. tube)	−5°17′	−11°26′	− 5°16′
Acid value	7·0	4·0	3·48
Total saponification value	31·7	23·2	17·98
Ester value	24·7	19·2	14·50
Saponification value of acetylated oil	—	56·4	50·23

Identification of the Constituents of the Oil.

For this purpose the oil obtained mainly from the leaves was subjected to examination. It has been stated that on cooling, or on addition of alcohol, a crystalline substance separates from the oil. To this is probably due the statement in the earlier work on the subject that the oil contains 70 per cent. of camphor. This latter should not be taken to mean the camphor of to-day, as this statement was probably made when the term "camphor" was applied to any solid substance separating from an oil. In any case, however, the amount present was considerably over-estimated. Messrs. Roure Bertrand Fils more correctly consider the separation of solid matter to be due to the presence of paraffins in the oil, but do not give any evidence in support of this conclusion.

In order to separate this constituent as far as possible, the oil (20 c.c.) was first cooled in a freezing mixture, and an equal volume of methyl alcohol was added. The crystalline solid which separated was collected, and washed with a little more methyl alcohol. It was then treated with a concentrated solution of sodium hydroxide for some time in order to remove entirely any acids, phenols, etc., and the undissolved material was finally dissolved in ether, from which it recrystallised in shining leaflets, melting at 63—64°.

This substance is apparently quite pure; it is almost insoluble in acetic anhydride, is not affected by potassium permanganate solution, and is scarcely acted on by sulphuric acid.

It is apparently a paraffin, having probably the composition $C_{29}H_{60}$. The quantity obtained from 20 c.c. oil was not more than 0·15 gram (about 0·75 per cent.). It is worthy of note that similar, if not identical, hydrocarbons have been found in the oils from certain *Pelargonium*, spp., *Cistus monspeliensis*, caraway (*Carum Carvi*, L.), dill (*Anethum graveolens*), *Arnica montana*, Indian hemp, etc.

The oil from which the solid portion had been removed was subjected to the following treatment. The methyl alcohol was removed by distillation and washing. The oil was then mixed with several volumes of ether, and the ethereal solution repeatedly

extracted with aqueous sodium carbonate solution. On acidifying the aqueous solution, a considerable quantity of solid material separated, which, after removal, drying, and recrystallising from alcohol, was obtained in glistening crystals, melting at 62°. It consisted almost entirely of palmitic acid.

The ethereal solution of the oil was afterwards treated with sodium hydroxide solution, but only a trace of indefinite material was removed by this means, and a subsequent treatment of the oil with sodium hydrogen sulphite solution also failed to separate any appreciable quantity of aldehydes or ketones.

After the removal of the ether the oil was subjected to distillation under diminished pressure, when the following fractions were obtained: (1) Small fraction, b. p. 76°/35 mm. (2) Fraction below 110°/20 mm. (3) Fraction 110—150°/20 mm. (4) Fraction 150—165°/20 mm. (5) Residue.

Fraction (1) had a pronounced odour of cineole, and the presence of this substance was definitely proved by the formation of its compound with tetraiodopyrrole (m. p. 112—114°). The cineole-tetraiodopyrrole compound is stated to melt at 112°.

Fraction (2) was redistilled under atmospheric pressure, when it was found to boil for the most part below 176°. The distillate had a terpene-like odour, together with that of cineole:

0·1210 gave 0·3770 CO_2 and 0·1260 H_2O. C=85·0; H=11·6.

This result seemed to indicate the presence of terpenes, together with cineole, and the presence of dipentene in this fraction was proved by the formation of dipentene tetrabromide. This was deposited from the oil in colourless plates after bromination, and when recrystallised from ethyl acetate melted at 124—125°.

The fractions of higher boiling point were first boiled with alcoholic potassium hydroxide to hydrolyse the esters present, and there was recovered from the potassium salts formed in this process a mixture of fatty acids insoluble in water. These acids, present in the oil in the form of esters, could not be separated and identified with certainty on account of the small quantity obtained. They were apparently of fairly high molecular weight, possibly nonoic or closely related acids.

After hydrolysis the oil was again fractionated: (1) Very small fraction, b. p. 180—220°. (2) Pale green liquid, b. p. 258—268°. (3) Pale blue liquid, b. p. 268—285°. (4) Residue of high boiling point.

Fraction b. p. 180—220°:—This had a somewhat menthol-like odour suggestive of a terpene alcohol:

0·1425 gave 0·4250 CO_2 and 0·1460 H_2O. C=81·4; H=11·4.

$C_{10}H_{18}O$ requires C=77·9; H=11·7 per cent.

This fraction probably consists of a terpene-alcohol mixed with a small proportion of terpenes. The quantity was, however, too small to attempt a separation, and attempts to obtain crystalline derivatives of the alcohol were unsuccessful.

Fraction b. p. 258—268°:—This was a pale green liquid, which yielded the following results on analysis:

0·1455 gave 0·4380 CO_2 and 0 1465 H_2O. C = 82·1; H = 11·2.

It had a pleasant, persistent odour, and it is to this fraction and the succeeding one, together with cineole, that the characteristic odour of the oil is due. A methoxyl determination was made on a portion of this fraction, but no methyl iodide was liberated.

Fraction b. p. 275—285°:—This was a fairly mobile liquid, having a pale blue colour and a pleasant odour:

0·1230 gave 0·3770 CO_2 and 0·1270 H_2O. C = 83·6; H = 11·5.

The two fractions b. p. 258—268° and b. p. 268—285° constitute about one-half of the total oil, and consist essentially of a sesquiterpene mixed with an oxygenated constituent, probably a higher alcohol.

On treatment of these fractions with hydrogen chloride only liquid hydrochlorides could be obtained. Unfortunately the small quantity of oil available did not allow of a more complete examination of this portion of the oil.

Summary.

The solid material which separates from the oil of *Myrica Gale* on cooling consists of a paraffin hydrocarbon, m. p. 63—64°, and probably having the formula $C_{29}H_{60}$, which is present to the extent of about 0·75 per cent.

The oil also contains (1) about 2·5 per cent. of free fatty acids, principally palmitic acid; (2) terpenes, including dipentene; (3) cineole; (4) esters of fatty acids; (5) probably a mixture of alcohols of high boiling point, and (6) a sesquiterpene.

The cineole and terpenes constitute approximately 50 per cent. of the oil.

SCIENTIFIC AND TECHNICAL DEPARTMENT,
IMPERIAL INSTITUTE, S.W.

CXCIX.—*An Application of Kirchhoff's Equation to Solutions. (A Contribution to the Thermodynamic Theory of Solubility.)*

By Robert Taylor Hardman and James Riddick Partington.

On the basis of his theory of solution, van't Hoff (*Kongl. Svenska. Akad. Handl.*, 1885, **21**, 38) deduced a general differential equation, applicable to solutions of all concentrations, which connects the osmotic pressure, P, of a saturated solution with λ^1, the latent heat of reversible dissolution in a saturated solution:

$$\frac{dP}{dT} = \frac{\lambda^1}{T\Delta V} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

ΔV = change of total volume occurring when enough solvent transpires through a semipermeable diaphragm to dissolve a gram-molecule of solute. If the system is maintained at a constant temperature T, and the external work $P\Delta V$ is done by the osmotic pressure, λ^1 is the heat absorbed in the process.

If λ is the heat absorbed when a molecule of solute dissolves in sufficient solvent to produce a saturated solution, so that no external work is done (say, by mixing the components in a calorimeter), then:

$$\lambda = \lambda^1 - P\Delta V \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Let us now assume that the osmotic pressure conforms to the laws of dilute solutions, so that:

$$P = \xi RT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where ξ = the volumetric molecular concentration of the solution, or the number of gram-molecules of solute per unit volume. By definition:

$$\xi = 1/\Delta V \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\therefore \frac{d\, ln}{dT}\xi = \frac{\lambda}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which is the general differential equation for saturated dilute solutions. The differential coefficients in (1) and (5) are total, since P and ξ are, under the conditions imposed, functions of T alone.

The integration of (5) was effected by van't Hoff on the assumption that λ may be regarded as sensibly constant over a small range of temperature $T_2 - T_1$, in which case one readily finds:

$$ln\frac{\xi_2}{\xi_1} = \frac{\lambda}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

an equation which gave satisfactory results in its own restricted

field (van Deventer and van der Staadt, *Zeitsch. physikal. Chem.*, 1892, **9**, 54; van Marseven, *ibid.*, 1895, **25**, 91; Noyes and Sammet, *ibid.*, 1903, **43**, 513). But if the range of temperature is not very small, the assumption about the constancy of λ is invalid.

The present authors have sought to extend the application of (5) to fairly large intervals of temperature, and for this purpose have utilised the well-known theorem of Kirchhoff (*Pogg. Ann.*, 1858, **103**) to the effect that the rate of increase of the heat of reaction, taken positive for heat absorbed, with the temperature at which a reaction proceeds, is equal to the total heat capacity of the system of products minus the total heat capacity of the system of initial substances:

$$\frac{dQ}{dT} = \Gamma^1 - \Gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Let s grams of solute saturate 100 grams of solvent, and let c_1, c_2, c be the specific heats of solute, solvent, and solution respectively. If Q is the heat absorbed in the calorimetric process:

$$\frac{dQ}{dT} = (s+100)c - (sc_1 + 100\,c_2) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The heat of solution increases, remains constant, or decreases with rise of temperature, according as:

$$(s + 100)c \gtreqless (sc_1 + 100\,c_2) \quad . \quad . \quad . \quad . \quad . \quad (9)$$

It appears that the lower inequality usually obtains.

If l is the heat absorbed when 1 gram of solute forms a saturated solution:

$$Q = sl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\therefore \frac{dl}{dT} = \frac{100 + s}{s}c - \frac{sc_1 + 100\,c_2}{s} \quad . \quad . \quad . \quad (11)$$

Now c_1, c_2, c may be assumed to be sensibly independent of temperature, so that:

$$l = l_0 + \frac{100 + s}{s}cT - \frac{sc_1 + 100\,c_2}{s}T$$

$$= l_0 + (c - c_1)\,T + \frac{100\,(c - c_2)}{s}T \quad . \quad . \quad . \quad (12)$$

where l_0 is an integration constant.

Now it has been shown experimentally by Schüller (1869), Thomsen (1870), and Marignac (1871–76) that the difference between the specific heats of the solution and solvent, in the case of dilute aqueous solutions, tends on increasing dilution to become proportional to the concentration. Assuming, therefore, in general:

$$c = c_2 + ks \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where k may be positive or negative, we have:

$$l = l_0 + (a_1 + a_2)T = l_0 + aT,$$

where $a_1 = c - c_1$, $a_2 = k$, $a = a_1 + a_2$, are constants. a is usually negative.

For a mol. (M grams) of solute we have:

$$\lambda = Ml = \lambda_0 - \alpha T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where $\alpha = -Ma$ is a constant.

The heat of solution is therefore a linear function of the temperature, and behaves similarly to the latent heat of evaporation of a pure liquid.

If we substitute (14) in (5), and integrate, we obtain:

$$ln\ \xi = \int \frac{\lambda_0 - \alpha T}{RT^2} dT = -\frac{\lambda_0}{RT} - \frac{\alpha}{R} lnT + C \quad . \quad (15)$$

where C is the integration constant.

The (hypothetical) physical significance of λ_0 and C is found by setting $T = 0$ in (14) and (15) respectively.

If we collect the constants, and multiply through by the modulus of the ordinary logarithms, we find:

$$\log \xi = A^1 - \frac{B}{T} - C \log T \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where A^1, B, C are constants:

$$B = -\frac{\lambda_0}{R} \times 2{\cdot}3026, \ C = \frac{M(a_1 + a_2)}{R} \times 2{\cdot}3026.$$

If ρ is the density of the solution, which we shall suppose does not differ appreciably from that of the pure solvent:

$$\xi = \frac{s\rho}{100M} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$\therefore \log s = A - \frac{B}{T} - C \log T \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where A is an arbitrary constant.

Equation (18) is exactly analogous to the vapour pressure equation variously called Dupré's, Rankine's, and Kirchhoff's, but first deduced by the latter:

$$\log p = A - \frac{B}{T} - C \log T.$$

The name of Rankine might more appropriately be associated with the equation:

$$\log p = \alpha - \frac{\beta}{T} - \frac{\gamma}{T^2} - \ . \ . \ .$$

(*Edin. Phil. Journ.*, 1849); the latter has recently been re-introduced, without any mention of Rankine, by E. Bose (*Physikal. Zeitsch.*, 1907, **8**, 944).

It is evident from the assumptions introduced in its deduction that equation (18) can, theoretically, be applied to dilute solutions only, just as Kirchhoff's equation should apply only to vapours at low pressures. Juliusburger (*Ann. Physik*, 1900, [iv], **3**, 618) finds that the latter equation applies, in the case of some sixty liquids, not only at low temperatures and correspondingly small vapour pressures (when the saturated vapours may be assumed to conform to the gas laws), but also even as far as the critical point. He therefore considers that it may, in those regions where thermodynamic theory cannot guarantee any support, still be regarded as a remarkably exact interpolation formula with three parameters.

The authors have applied the equation (18) to the solubility data for some organic substances in organic solvents (Tyrer, Trans., 1910, **97**, 1778), and for sucrose in water (Landolt-Börnstein, *Tabellen*).

With the exception of one value in table III, the observed and calculated results agree to 0·7 per cent., and the differences are usually much less. This agreement is all the more remarkable when one considers that the more concentrated solutions—or rather syrups—contain as much as three parts by weight of sucrose to one of water, and cannot therefore be regarded in any way as "dilute." The analogy between solution and evaporation is here strikingly seen.

No assumptions have been made in the above argument as to the condition of the solute, and, as has been previously observed by one of us (Partington, Trans., 1910, **97**, 1158), such considerations are quite foreign to the spirit of the theory. In particular, equation (3) is not taken to imply any identity, or even physical similarity, between the state of the solute and that of a free gas. The real fundamental proposition of the thermodynamic theory of solution is contained in the assertion that the osmotic pressure of a solution, and every other property conditioned solely by it, depend simply on the number of solute molecules scattered through a given volume of solution, and not at all on the chemical nature of either solute or solvent, or on the relation between the latter, provided only that the solution is dilute. The chemical properties of solutions, on the contrary, depend, not only on the number, but also on the nature of the dispersed particles, and so are to a large extent conditioned by the exact mode of connexion between the solvent and solute.

It seems necessary to emphasise this point because of the fallacy, which unfortunately appears to be widely spread, that there is some fatal incompatibility between the old qualitative hydrate theory of solution and the new quantitative thermodynamic theory of which

van't Hoff was the pioneer. This view has resulted from the one-sided outlook of the champions of each theory, and is certainly not a necessary consequence of the fundamental basis of either. It is greatly to be desired that writers on the theory of solution should distinguish clearly exactly which aspect of the subject belongs properly to their own investigations, and should refrain from attaching, on the basis of irrelevant experiments, a theory which is quite immune from the criticism which may reasonably be levelled against any particular hypothetical view of the nature of solutions.

The authors also find themselves unable to accept the statements of Tyrer (*loc. cit.*) to the effect that: "With non-associated solvents there is evidence for the belief that the solute (if it is not associated) does not associate with the solvent, but the molecules of both move freely among each other like the molecules of a mixed gas." Also: "In the majority of aqueous solutions, and in all cases where the solvent is an associated liquid, as, for example, a solvent containing a hydroxyl group, molecular association of the solvent and solute undoubtedly occurs, and the process of dissolution in these cases is probably due to these complex molecules." Apart from the use of "association" in more than one sense in this passage, it does not appear to render by any means obvious why two substances, which are not associated separately, should not combine when brought together, and certainly affords no reason why there should "undoubtedly" be combination if one substance happens to be associated.

The same author has introduced a magnitude which he calls the "concentration of the solvent," and defines as the number of grams of solvent in 1 c.c. of solution. The importance of this quantity appears, however, to have been over-estimated. The solubility of a substance is represented as a function of T, and the concentration of the solvent, C:

$$s=\phi(T,C).$$

[Tyrer's equation:

$$s=kf(T)\phi(C),$$

is an unnecessary divergence from standard mathematical usage.]

No new conception appears thereby to be introduced, as can be seen most simply if we remember that s and C are not independent, and that the equation therefore reduces to the well-known form:

$$s=f(T)$$

at constant pressure.

In the present paper it is shown that an expression for $f(T)$ can be derived, which agrees with the experimental data.

If the pressure is not constant, an increase of pressure must, if the system is real, give rise to an increase of C, and therefore (since

the solubility should increase with the latter unless very improbable properties of C are assumed) should invariably increase the solubility. This is by no means the case.

Experimental.

All the solubilities are expressed in terms of the number of grams of solute per 100 grams of solvent in the saturated solution.

(1) *Anthraquinone in Benzene.*

$A = -44{\cdot}369$. $B = -805{\cdot}111$. $C = -16{\cdot}6262$.

Temp. abs.	Obs. *s*.	Calc. *s*.	Difference.
283	0·173	0·173	—
293	0·256	0·247	+0·009
303	0·350	0·350	0·000
313	0·495	0·495	—
323	0·700	0·695	+0·005
333	0·974	0·972	+0·002
343	1·355	1·355	—

(2) *Anthraquinone in Chloroform.*

$A = -2{\cdot}479$. $B = 748{\cdot}8079$. $C = -1{\cdot}9516$.

Temp. abs.	Obs. *s*.	Calc. *s*.	Difference.
283	0·457	0·457	—
293	0·605	0·602	+0·003
303	0·780	0·780	—
313	0·994	0·997	−0·003
323	1·256	1·256	—
333	1·577	1·567	−0·010

(3) *Anthracene in Benzene.*

$A = -7{\cdot}1236$. $B = 1466{\cdot}751$. $C = 0{\cdot}7960$.

Temp. abs.	Obs. *s*.	Calc. *s*.	Difference.
283	0·975	0·975	—
293	1·43	1·425	−0·005
303	2·03	2·03	—
313	2·78	2·82	+0·04
323	3·75	3·84	+0·09
333	5·14	5·14	—
343	7·00	6·75	−0·25

(4) *Phenanthraquinone in Benzene.*

$A = -99{\cdot}126$. $B = 3450{\cdot}512$. $C = -35{\cdot}3$.

Temp. abs.	Obs. *s*.	Calc. *s*.	Difference.
283	0·412	0·412	±0·000
293	0·538	0·538	—
303	0·730	0·719	−0·019
313	1·032	0·979	−0·053
323	1·354	1·354	—
333	1·760	1·89	+0·13
343	2·687	2·687	—
353	3·77	3·86	+0·09

(5) *Sucrose in Water.*

$A = -32{\cdot}235.\quad B = -1283{\cdot}65.\quad C = -12{\cdot}2267.$

Temp. abs.	Obs. *s*.	Calc. *s*.	Difference.
273	179·2	179·2	—
283	190·5	189·8	−0·7
293	203·9	203·2	−0·7
303	219·5	219·5	—
313	238·1	239·8	+1·7
323	260·4	262·0	+1·6
333	287·3	288·4	+1·1
343	320·5	320·5	—

CHEMICAL DEPARTMENT,
UNIVERSITY OF MANCHESTER.

CC.—*The Action of Benzylamine on* s-*Dibromosuccinic Acid.*

By EDWARD PERCY FRANKLAND.

HITHERTO no experiments have been carried out on the action of aliphatic amines on symmetric dibromosuccinic acid, although the reaction with ammonia has been studied by several investigators with somewhat contradictory results. Thus Lindner and Lehrfeld (*Ber.*, 1881, **14**, 1816), acting on dibromosuccinic acid with alcoholic ammonia, obtained a small quantity of a diaminosuccinic acid decomposing at 200°, and practically insoluble in water, alcohol, or ether. This result was challenged by Claus (*Ber.*, 1882, **15**, 1849), who, working under the same conditions, obtained an almost theoretical yield of an intermediate product, namely, the ammonium salt of bromoaminosuccinic acid, $CO_2H{\cdot}CH(NH_2){\cdot}CHBr{\cdot}CO_2H$, together with a minute quantity of ammonium diaminosuccinate. By the saponification of an ester prepared by the action of alcoholic ammonia on dibromosuccinic ethyl ester, Claus and Helpenstein (*Ber.*, 1881, **14**, 624) isolated a substance having the constitution of diaminosuccinic acid, but with properties differing from those of Lindner and Lehrfeld's acid; for example, this compound melted at 151°, and was soluble in water, alcohol, or ether. Lehrfeld showed, however (*Ber.*, 1881, **14**, 1816), that the action of alcoholic ammonia on dibromosuccinic ester gives rise, not to diaminosuccinic ester, but to iminosuccinamic ester, $NH<\begin{matrix}CH{\cdot}CO{\cdot}NH_2\\ |\\ CH{\cdot}CO_2Et\end{matrix}$, a result confirmed by Hell and Poliakoff (*Ber.*, 1892, **25**, 640).

Lindner and Lehrfeld's diaminosuccinic acid was subsequently

prepared in larger quantity by Tafel (*Ber.*, 1887, **20**, 247; 1893, **26**, 1980) by the reduction of tartaric acid phenylhydrazone and osazone. In this case two isomeric acids were produced, one of which, apparently identical with Lindner and Lehrfeld's acid, yielded *i*-tartaric acid with nitrous acid, whereas the other, which was more soluble in water, acid, and alkali, and crystallised with one molecule of water, gave rise to racemic acid.

The action of aniline on dibromosuccinic acid has been studied by Reissert (*Ber.*, 1893, **26**, 1758), who isolated three distinct substances, which he formulated as:

$$\begin{array}{l} NPh\cdot CH\cdot CO_2H \\ \;| \qquad | \\ CO—CH\cdot NHPh \end{array} \qquad \begin{array}{l} NPh\cdot CH\cdot CO \\ \;| \qquad | \qquad | \\ CO—CH\cdot NPh \end{array} \qquad \text{and} \qquad \begin{array}{l} CH\cdot NHPh \\ \;|| \\ CH\cdot CO_2H \end{array}$$

(I.) (II.) β-Anilinoacrylic acid. (III.)

The first of these can be hydrolysed with sodium hydroxide to give a dianilinosuccinic acid, apparently identical with that prepared by Gorodetzki and Hell (*Ber.*, 1888, **21**, 1795) from dianilinosuccinic ethyl ester.

Reissert and Junghahn (*Ber.*, 1893, **26**, 1766) have shown that *p*-toluidine yields derivatives with dibromosuccinic acid exactly analogous to the anilino-derivatives mentioned above.

In examining the action of benzylamine on dibromosuccinic acid, the author has obtained different results according as the solvent used was water or alcohol. The course of the reaction can be followed more easily in the latter solvent, owing to the comparatively sparing solubility in alcohol of the various substances liable to be formed. The reaction proceeds, as might be expected, in a manner more analogous to the case of ammonia than to that of aniline, and bears a general resemblance to the reaction described by Claus (*Ber.*, 1882, **15**, 1849). A benzylaminobromosuccinic acid (benzylamine salt) appears during the early stages of the reaction, but is gradually converted into a dibenzylamino-acid, which in its properties closely resembles the diaminosuccinic acid described by Lehrfeld and by Tafel. The displacement of the second bromine atom by a benzylamino-group thus proceeds with much greater ease than in the case of the amino-group. Whereas Lehrfeld obtained only 4 grams of diaminosuccinic acid from 200 grams of dibromosuccinic acid, the author was able to prepare 7·2 grams of dibenzylaminosuccinic acid (monobenzylamine salt) from 8 grams of dibromosuccinic acid, corresponding with a yield of 57 per cent.

On mixing alcoholic solutions of benzylamine and dibromosuccinic acid, the dibenzylamine salt of dibromosuccinic acid separated in the course of a few minutes. When this substance was recrystallised from alcohol, it underwent a change, losing hydrogen bromide, and

yielding presumably the monobenzylamine salt of bromomaleic acid. If the reaction mixture, which contained 4 molecules of amine to one of acid, was heated on the water-bath, another product was deposited; this was found to consist of two distinct substances, one melting at 156—157°, the other decomposing at 232°. The substance of low melting point was found, on analysis, to be the monobenzylamine salt of benzylaminobromosuccinic acid,

$$CO_2H\cdot CH(NH\cdot C_7H_7)\cdot CHBr\cdot CO_2H.$$

Both this substance and the benzylamine salt of bromomaleic acid are stable when heated with alcohol, but are slowly converted into the substance decomposing at 232° when a few drops of benzylamine are added to the boiling solution. On analysis, this substance appeared to be the monobenzylamine salt of dibenzylaminosuccinic acid, $CO_2H\cdot CH(NH\cdot C_7H_7)\cdot CH(NH\cdot C_7H_7)\cdot CO_2H$. The course of the reaction may be illustrated by the following equations:

$$(1)\quad \begin{array}{l} CHBr\cdot CO_2H \\ | \\ CHBr\cdot CO_2H \end{array} + 2C_7H_7\cdot NH_2 = \begin{array}{l} CHBr\cdot CO_2H,C_7H_7\cdot NH_2 \\ | \\ CHBr\cdot CO_2H,C_7H_7\cdot NH_2 \end{array}.$$

$$(2)\quad \begin{array}{l} CHBr\cdot CO_2H,C_7H_7\cdot NH_2 \\ | \\ CHBr\cdot CO_2H,C_7H_7\cdot NH_2 \end{array} = \begin{array}{l} CBr\cdot CO_2H \\ \| \\ CH\cdot CO_2H,C_7H_7\cdot NH_2 \end{array} + C_7H_7\cdot NH_3Br.$$

$$(3)\quad \begin{array}{l} CBr\cdot CO_2H \\ \| \\ CH\cdot CO_2H,C_7H_7\cdot NH_2 \end{array} + C_7H_7\cdot NH_2 = \begin{array}{l} CHBr\cdot CO_2H,C_7H_7\cdot NH_2 \\ | \\ CH(NH\cdot C_7H_7)\cdot CO_2H \end{array}.$$

$$(4)\quad \begin{array}{l} CHBr\cdot CO_2H,C_7H_7\cdot NH_2 \\ | \\ CH(NH\cdot C_7H_7)\cdot CO_2H \end{array} + 2C_7H_7\cdot NH_2 =$$
$$\begin{array}{l} CH(NH\cdot C_7H_7)\cdot CO_2H \\ | \\ CH(NH\cdot C_7H_7)\cdot CO_2H,C_7H_7\cdot NH_2 \end{array} + C_7H_7\cdot NH_3Br.$$

The first equation represents the formation of a precipitate of the dibenzylamine salt of dibromosuccinic acid, which, in the second equation, is converted into the monobenzylamine salt of bromomaleic acid. The third equation shows the probable method of formation of the monobenzylamine salt of benzylaminobromosuccinic acid, a substance which also has a transitory existence in the reaction mixture when heated on the water-bath under reflux, passing into the final product, the monobenzylamine salt of dibenzylaminosuccinic acid as shown in the fourth equation.

The free acid can be obtained from the crude benzylamine salt by dissolving the latter in concentrated hydrochloric acid and precipitating with water. Benzylamine hydrochloride remains in the aqueous solution, and the yield of free acid from the amine salt corresponds with theory.

When benzylamine was allowed to react on dibromosuccinic acid in aqueous solution, two products were obtained, one of which was soluble in ammonia, and proved, on analysis, to be the dibenzyl-

amine salt of dibenzylaminosuccinic acid, the other, insoluble in ammonia and melting at 203—207°, gave, on analysis, figures indicating the formula $C_{18}H_{20}O_4N_2$. This substance possessed properties quite unlike those of the isomeric dibenzylaminosuccinic acid, and it was found to be identical with the dibenzylamide of *i*-tartaric acid prepared by the author by heating together benzylamine and *i*-tartaric acid. The dibenzylamide of racemic acid was also prepared; it melted at practically the same temperature as the *i*-compound, but gave a considerable lowering of the melting point when mixed with the product obtained from dibromosuccinic acid. Apparently the formation of a tartramide derivative from *i*-dibromosuccinic acid is not accompanied by a Walden inversion, as otherwise we should expect a benzylamide of racemic acid to be produced.

The only dibenzylamide of tartaric acid known hitherto was prepared by P. Frankland and Slator (Trans., 1903, **83**, 1362) from methyl *d*-tartrate. It is described as crystallising in white, glistening plates, soluble in alcohol, insoluble in water, and melting at 199°.

Lutz (*Diss.*, Rostock; Abstr., 1901, i, 7) has shown that both ammonia and benzylamine react on monohalogen succinic acids to form monoamides of malic acid instead of the expected aspartic acids. Thus, *l*-monobromosuccinic acid with benzylamine yields the benzylamine salt of *d*-β-benzylmalamic acid,

$$CO_2H\cdot CH(OH)\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7,$$

presumably owing to migration of oxygen from the carboxyl group to the β-position during the removal of bromine as benzylamine hydrobromide. An analogous reaction in the case of dibromosuccinic acid would lead to the dibenzylamide of a tartaric acid; most probably *i*-tartaric acid, since *s*-dibromosuccinic acid yields principally a diaminosuccinic acid, which, according to Tafel, is converted by nitrous acid into *i*-tartaric acid.

Experimental.

I.—*Action of Benzylamine on Dibromosuccinic Acid in Ethyl-Alcoholic Solution.*

(*a*) A solution of 6·2 grams of dibromosuccinic acid in 70 c.c. of absolute ethyl alcohol was treated with 10 grams of benzylamine. The solution became warm, and a crystalline precipitate was thrown down. This was collected and washed with alcohol and ether; after drying in the steam-oven, it weighed 10·4 grams. Theory requires 11·0 grams of the dibenzylamine salt of dibromosuccinic acid. The substance crystallised in well-defined prisms, and melted without charring at 149°.* It contained no ionic bromine:

* All temperatures here given are uncorrected.

0·1089 gave 88·81 c.c. CO_2 and 4·91 c.c. N_2.* C=43·87; N=5·66.
0·2497 „ 0·1919 AgBr. Br=32·70.

$C_{18}H_{22}O_4N_2Br_2$ requires C=44·08; N=5·71; Br=32·65 per cent.

A portion of the substance was dissolved in absolute alcohol. After some time, the solution deposited large, broad, prismatic plates and needles, which melted at 145°. The mother liquor contained ionic bromine. This substance, the *monobenzylamine* salt of *bromomaleic acid*, dissolved readily in water and in alcohol, and the aqueous solution decolorised permanganate instantly in the cold:

0·1036 gave 83·35 c.c. CO_2 and 3·97 c.c. N_2. C=43·75; N=4·82.
0·1255 „ 101·75 c.c. CO_2 „ 4·63 c.c. N_2. C=43·65; N=4·63.

$C_{11}H_{11}O_4NBr$ requires C=43·71; N=4·64 per cent.

When a small quantity of the substance was heated in alcoholic solution with a few drops of benzylamine for about half an hour on the water-bath, a precipitate began to form. After about one hour's heating, the precipitate was collected, and washed with alcohol and ether. It decomposed at 236°. After dissolving in concentrated hydrochloric acid and precipitating with water, the substance decomposed at 251°, and crystallised from aqueous ammonia in stellate aggregates of prisms (dibenzylaminosuccinic acid). The acid mother liquor yielded crystals of benzylamine hydrochloride (m. p. 253°).

(*b*) A solution of 5 grams of dibromosuccinic acid in 70 c.c. of absolute alcohol was treated with 8 grams of benzylamine. On heating on the water-bath, the precipitate formed on mixing dissolved, and after about fifteen minutes another precipitate began to deposit. The solution was then cooled, the precipitate collected, and washed with alcohol and ether. After drying in the steam-oven, it weighed 5·9 grams. A specimen melted and decomposed at 160°, and contained no ionic bromine. The substance was boiled with absolute alcohol, the insoluble portion collected and washed with hot alcohol, and finally with ether. After drying in the steam-oven, this portion weighed 1·15 grams. It decomposed at 232° [compare experiment (*c*)]. On cooling the alcoholic solution and washings, a crystalline substance separated out. It was washed with a little alcohol and with ether, and after drying weighed 2·22 grams. This substance contained no ionic bromine; it crystallised in rectangular plates, melting at 156—157°, which were readily soluble in water, but sparingly so in cold alcohol; the aqueous solution did not decolorise permanganate in the cold. Most

* (Carbon and nitrogen combustion in a vacuum.) All gas volumes are corrected to N.T.P.

probably this substance is the *monobenzylamine* salt of *benzylaminobromosuccinic acid*:

0·0893 gave 87·47 c.c. CO_2 and 5·00 c.c. N_2. C = 52·64; N = 7·04.
0·2724 „ 0·1237 AgBr. Br = 19·32.

$C_{18}H_{20}O_4N_2Br$ requires C = 52·81; N = 6·85; Br = 19·56 per cent.

This substance apparently could not be converted into dibenzylaminosuccinic acid by boiling with alcohol, but on adding a drop of benzylamine and heating for three-quarters of an hour on the water-bath, a white precipitate was formed similar to that appearing in the reaction mixture of benzylamine and dibromosuccinic acid on continued heating. It decomposed at 242°, and crystallised from aqueous ammonia in the groups of prismatic crystals characteristic of dibenzylaminosuccinic acid.

(*c*) A solution of 5 grams of dibromosuccinic acid in 70 c.c. of absolute alcohol was heated to boiling with 8 grams of benzylamine. The precipitate formed was collected from time to time, washed with hot alcohol, and the washings returned to the mother liquor. In this way, the more soluble benzylaminobromosuccinic acid (benzylamine salt) was submitted to the continued action of alcoholic benzylamine. The first fraction, collected after one hour's heating, weighed 2·85 grams, and decomposed at 238°. The second fraction, collected after another hour's heating, weighed 1·13 grams, and decomposed at 242°.

The mother liquor was finally evaporated to dryness, and the residue dissolved in water. A quantity of benzylamine hydrobromide passed into solution, and the insoluble portion was collected and washed with alcohol, whereby some brown, tarry matter was removed. The total weight of insoluble product obtained from this experiment was 4·9 grams. Theory requires 7·9 grams of the *monobenzylamine* salt of *dibenzylaminosuccinic acid*:

0·0704 gave 89·46 c.c. CO_2 and 5·53 c.c. N_2. C = 68·45; N = 9·88.
0·0884 „ 6·91 c.c. N_2. N = 9·82.

$C_{25}H_{29}O_4N_3$ requires C = 68·96; N = 9·65 per cent.

This substance was very sparingly soluble in water or alcohol, readily so in concentrated acids and in aqueous ammonia. Both acids and ammonia removed benzylamine from the molecule, and from the hydrochloric acid mother liquor, crystalline plates of benzylamine hydrochloride (m. p. 254°) could be isolated. The substance crystallising out from acid on dilution, or from ammonia on concentration, was dibenzylaminosuccinic acid. From the latter solvent it appeared in small, spherical aggregates of acicular prisms, which decomposed at 251°. Some specimens, even after repeated recrystallisation, decomposed at as low a temperature as 249°, others not below 253°.

Four grams of the benzylamine salt of dibenzylaminosuccinic acid were dissolved in concentrated hydrochloric acid, the solution was diluted with a large volume of water, and the resulting precipitate collected, washed with water, alcohol and ether, and dried. It weighed 3 grams. Theory requires 3 grams of *dibenzylaminosuccinic acid.*

The substance was practically insoluble in water, alcohol, or ether, but, like its benzylamine salt, was readily dissolved by concentrated acids and by aqueous ammonia:

0·0801 (dec. 253°) gave 97·61 c.c. CO_2 and 5·49 c.c. N_2. C=65·43; N=8·62.

0·0847 (dec. 250—251°) gave 102·84 c.c. CO_2 and 5·84 c.c. N_2. C=65·56; N=8·66.

$C_{18}H_{20}O_4N_2$ requires C=65·86; N=8·54 per cent.

The solution of this substance in a small volume of concentrated hydrochloric acid occasionally solidified to a crystalline mass which did not redissolve on adding excess of acid, but passed into solution in warm water. The aqueous solution almost instantly deposited the free dibenzylaminosuccinic acid. The substance separating from the acid solution was collected, and freed from hydrochloric acid by washing with ether, and finally by keeping in a vacuum over soda-lime and sulphuric acid. It melted and decomposed at 165°, and gave, on analysis, figures indicating approximately the composition of a *dihydrochloride* of *dibenzylaminosuccinic acid*:

0·2022 gave 0·1402 AgCl. Cl=17·16.
0·2063 „ 0·1430 AgCl. Cl=17·15.

$C_{18}H_{20}O_4N_2,2HCl$ requires Cl=17·71 per cent.

II.—*Action of Benzylamine on Dibromosuccinic Acid in Aqueous Solution.*

A solution of 8 grams of dibromosuccinic acid in 100 c.c. of water was treated with 12·4 grams of benzylamine (six molecules). The solution became warm. It was heated to boiling under reflux, and became cloudy after about ten minutes. After about half an hour's heating, a yellow, tarry product appeared, and a precipitate of small, glancing plates was deposited. The heating was continued, and a white, flocculent precipitate appeared in addition to the plates. The solution was filtered hot after one and a-half hours' heating, and the product washed with water, alcohol, and ether. It weighed 2·7 grams, and decomposed at 212°. The filtrate was heated for two and a-quarter hours longer, when a second fraction was obtained, weighing 1·7 grams, and decomposing at 225°. Another hour's heating yielded only 0·15 gram of product.

The products thus obtained were warmed with aqueous ammonia. The precipitate of small plates remained undissolved, and was collected, washed with water, with alcohol to remove tar, and finally with ether. After drying, it weighed 0·85 gram. The substance had a pale green tinge, and melted at 203°. After recrystallisation from a large volume of alcohol, it appeared in small, colourless, rhomboidal plates, melting at 203—207°, practically insoluble in water, sparingly soluble in alcohol, insoluble in ammonia, and only slowly dissolved by hot concentrated hydrochloric acid. Two other experiments, one with 3·8 grams, the other with 5 grams of dibromosuccinic acid, with 4 molecules of amine, yielded 0·6 and 0·7 gram respectively of this substance, the *dibenzylamide* of tartaric acid:

0·0814 gave 99·46 c.c. CO_2 and 5·59 c.c. N_2. C = 65·78; N = 8·62.
0·1916 „ 0·4610 CO_2 and 0·1100 H_2O. C = 65·63; H = 6·38.
$C_{18}H_{20}O_4N_2$ requires C = 65·86; H = 6·10; N = 8·54 per cent.

A portion of this substance was dissolved by prolonged boiling with concentrated hydrochloric acid, and the solution was evaporated to a syrup and stirred with alcohol. A precipitate of crystalline plates was collected and recrystallised from alcohol. On examination, this substance was shown to be benzylamine hydrochloride. It melted at 253°, and contained ionic chlorine. (Found, C = 58·79; N = 9·79. Calc., C = 58·54; N = 9·76 per cent.)

In order to compare the product melting at 203—207° with the dibenzylamides of *i*-tartaric and racemic acids respectively, these substances were synthesised by heating together the respective acids with benzylamine (2 molecules) for seven and a-half and nine and a-half hours at 130° to 150°. The resulting products were purified by repeated recrystallisation from alcohol.

The *dibenzylamide* of *i*-tartaric acid crystallised from alcohol in small, rhomboidal plates, which melted at 203—205°:

0·0838 gave 102·42 c.c. CO_2 and 5·86 c.c. N_2. C = 65·83; N = 8·78.
$C_{18}H_{20}O_4N_2$ requires C = 65·86; N = 8·54 per cent.

A mixture of this substance with the product obtained from dibromosuccinic acid melted at 203—207°.

The *dibenzylamide* of racemic acid crystallised from alcohol in rhomboidal plates, similar to the above, which melted at 206—207°:

0·0842 gave 102·45 c.c. CO_2 and 5·85 c.c. N_2. C = 65·55; N = 8·72.
$C_{18}H_{20}O_4N_2$ requires C = 65·86; N = 8·54 per cent.

A mixture of this substance with the product obtained from dibromosuccinic acid melted at 192—195°.

Hence the product from dibromosuccinic acid is the dibenzylamide of *i*-tartaric acid, not of racemic acid.

It was observed that the dibenzylamide of *i*-tartaric acid, whether

prepared from *i*-tartaric acid or from dibromosuccinic acid, was coloured yellow on melting, whereas the dibenzylamide of racemic acid remained practically colourless.

The ammoniacal extract of the reaction product from benzylamine and dibromosuccinic acid was concentrated to a small bulk, whereupon a substance separated out, which decomposed at 221°. After two recrystallisations from hydrochloric acid and water a product was obtained, decomposing at 250°, and having the characteristic appearance of dibenzylaminosuccinic acid.

In another experiment the product crystallising out after the tartramide derivative had been removed was recrystallised from hot water containing a few drops of benzylamine. The substance dissolved only sparingly in hot water alone, but the solubility was much greater than that of the monobenzylamine salt of the dibenzylamino-acid obtained in alcoholic solution. It separated from the aqueous benzylamine solution in prisms, which melted and decomposed at 226—227°. On analysis this substance proved to be the *dibenzylamine* salt of *dibenzylaminosuccinic acid*:

0·0797 gave 104·46 c.c. CO_2 and 6·56 c.c. N_2. C = 70·58; N = 10·35.
$C_{32}H_{38}O_4N_4$ requires C = 70·85; N = 10·31 per cent.

In another experiment the above product, after filtration from the reaction mixture, was treated with boiling aqueous alcohol. The greater part passed into solution, leaving a small residue of white, crystalline substance, decomposing at 232°. On analysis this compound was shown to have the composition of free dibenzylaminosuccinic acid. (Found, C = 65·65; N = 8·75. Calc., C = 65·86; N = 8·54 per cent.)

CHEMICAL DEPARTMENT,
THE UNIVERSITY, EDGBASTON, BIRMINGHAM.

CCI.—*A Method of Determining Carbon and Nitrogen in Organic Compounds.*

By EDWARD PERCY FRANKLAND.

THE Frankland-Armstrong vacuum combustion process (*Journ. Chem. Soc.*, 1868, **21**, 77), originally designed for the determination of minute quantities of carbon and nitrogen in water analysis, can be adapted for the determination of carbon and nitrogen in organic compounds without having recourse to the usual apparatus for gas analysis. This method is in use in a very few chemical laboratories

for the estimation of nitrogen, but, so far as the author is aware, it has not been customary to collect and measure the carbon dioxide evolved, and thus by means of a single combustion to determine both nitrogen and carbon.

Besides the Sprengel pump, the only apparatus necessary is a couple of glass measuring tubes graduated in tenths of a c.c., one of about 150 c.c. capacity, the other 50 c.c. or less, together with glass cylinders, in which the tubes may be levelled over mercury and water respectively.

The operation can be performed in considerably less time than that required for an ordinary carbon-hydrogen combustion; only one weighing is necessary (that of the substance taken for combustion), and satisfactory results can be obtained by the combustion of 0·1 gram of substance and even less.

The figures obtained by this method for a variety of organic substances containing nitrogen are generally more accurate than the average of figures obtained by the ordinary carbon-hydrogen combustion process. The method is of special utility in the case of a preliminary analysis of a substance of unknown constitution, figures for carbon and nitrogen being generally of greater value in fixing a formula than those for carbon and hydrogen. The results obtained by this method of analysis are not affected by the presence of halogens, a substance containing over 80 per cent. of bromine yielding very nearly theoretical figures for nitrogen and carbon; hence this process appears to be of especial advantage in connexion with substances containing both nitrogen and halogen.

The substance to be analysed is mixed with fine copper oxide, and introduced into a combustion tube (closed at one end), which is then filled with the usual length of coarse copper oxide. A reduced copper spiral is fitted in, and the tube is then drawn out before the blow-pipe, attached to the Sprengel pump, and exhausted. During the last stages of the exhaustion some burners are lighted below the copper spiral. The combustion is carried out in the ordinary manner, and the gas evolved is collected over mercury in a glass vessel graduated in tenths of a c.c., closed by a tap at one end. When the gas has ceased to pass over, the combustion tube is thoroughly exhausted with the pump, and the measuring vessel transferred to a cylinder of mercury in a room free from draughts. The temperature is registered by a sensitive thermometer hanging beside the glass vessel, and the volume of gas at atmospheric pressure is read off through a telescope. This measurement gives the volume of moist carbon dioxide and nitrogen.

The gas is now treated with strong aqueous potassium hydroxide introduced through a bent pipette to absorb carbon dioxide, and

when the liquid has remained at the same level for ten minutes with occasional shaking, it is allowed to diffuse out into water recently boiled to free it from dissolved air. The residual gas (nitrogen) is then expelled through the glass tap (by sinking the measuring vessel in a cylinder of water) into a narrow glass measuring tube graduated in tenths of a c.c. This is necessary, as it was found convenient to have the upper portion of the large measuring vessel ungraduated and expanded to take a large volume of gas, thus reducing the length of the apparatus.

The nitrogen gas is finally measured over water, and the weights of nitrogen and of carbon dioxide determined by reference to density tables.

Below are given the details of a combustion of β-γ-dibromopropylamine hydrobromide:

0·3129 gave 104·5 c.c. CO_2+N_2 at 16·8° and 647 mm. Volume of N_2 after absorption with KOH = 12·8 c.c. at 16·8° and 756 mm. C = 12·08; N = 4·73.

$C_3H_8NBr_3$ requires C = 12·08; N = 4·70 per cent.

The results of other combustions carried out by this method will be found in the preceding paper.

CHEMICAL DEPARTMENT,
THE UNIVERSITY, EDGBASTON, BIRMINGHAM.

CCII. — *The Absorption Spectra of the Isomeric Hydrazones and Semicarbazones of Camphorquinone.*

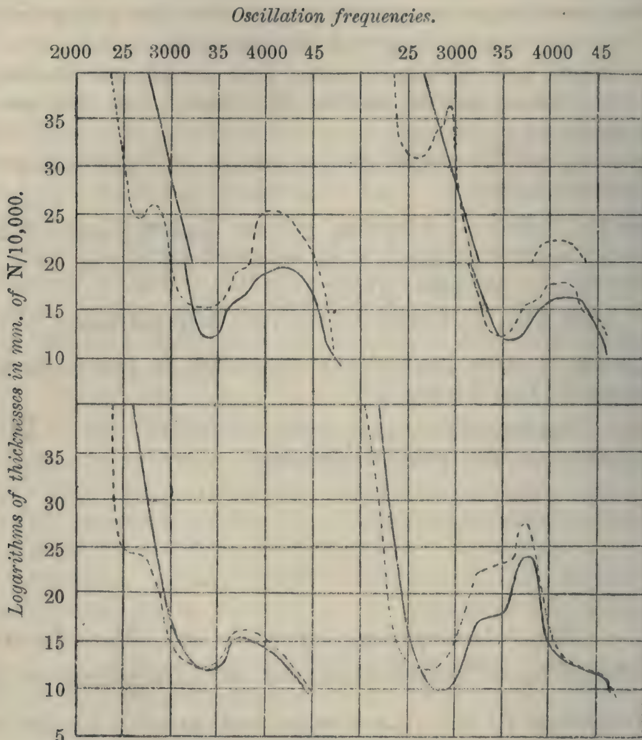
By FREDERICK RUSSELL LANKSHEAR and ARTHUR LAPWORTH.

FORSTER and Zimmerli have recently shown that the products obtained by the condensation of camphorquinone with hydrazine, semicarbazide, phenylcarbamylhydrazide, and phenylhydrazine can exist in two isomeric forms in each case (Trans., 1910, **97**, 2156; this vol., 478). The properties of the compounds appeared to point unmistakably to the conclusion that both forms must be regarded as conventional hydrazones with azethenoid linkings, and consequently the existence of stereoisomerism in the sense of the Hantsch-Werner hypothesis was inferred.

Certain definite characteristics of the members of each pair led Forster and Zimmerli to classify one of each as an α-derivative and the other as a β-derivative, a similar spacial relationship being

supposed to subsist between the four representatives of each class respectively.

We are much indebted to Dr. Forster, who kindly gave us the opportunity of comparing the absorption spectra of these eight compounds, and our results are shown in the appended figures. As usual, the depths of the solution varied from 10 mm. to 100 mm.,



Upper curves (left) *Camphorquinonehydrazones.*
(right) *Camphorquinonesemicarbazones.*

Lower curves (left) *Camphorquinonephenylcarbamylhydrazones.*
(right) *Camphorquinonephenylhydrazones.*

The full curves refer to the α-modifications and the others to the β-modifications.

and in each case three solutions, $N/100$, $N/1000$, and $N/10{,}000$ respectively, were examined.

Each of the β-representatives, except in the case of the phenylhydrazone, shows an irregularity at 2600—2700, which in the case of the hydrazone develops to a shallow band with its head at 2718, and in that of the semicarbazone to a moderately deep one with its head at 2950. There is no sign of such irregularities in the case

of the corresponding α-compounds. The β-series, moreover, are uniformly less transparent to the longer wave-lengths (below 2700—3400), but more transparent to wave-lengths shorter than these, and the persistence is invariably somewhat greater than in the α-series. Apart from these points there is a general resemblance between the spectra of the two members of each pair, and the principal bands have their heads comparatively near one another, at 2800—3600. It should be added that the absorption spectrum of the α-phenylhydrazone has already been examined by Baly, Tuck, Marsden, and Gazdar (Trans., 1907, **91**, 1572), the curve of which corresponds closely with that shown above, except that the short and nearly horizontal portion at 3200—3500 in the above diagram is seen in the earlier figure as a shallow band.

The absorption spectra of the camphorquinone derivatives exhibit conspicuous deviations from Beer's law, and this is most marked in the case of the β-semicarbazone, as the diagram shows sufficiently clearly.

It seems almost beyond question that the α-compounds form one series, and the β-compounds another, as was inferred by Forster and Zimmerli, the general relations of the pairs being of much the same character throughout; it appears highly probable that whatever be the nature of the isomerism between the members of one pair, the same explanation must be given for each of the other three pairs. It would be premature in our present state of knowledge of the relationship between chemical constitution and absorption spectra to suggest that the spectroscopic results throw any light on the nature of the isomerism, but there is nothing which tends to weaken the case made out by Forster and Zimmerli in favour of the application of the Hantsch-Werner hypothesis to the case. The close general resemblance between the ultraviolet absorption spectra of the phenylhydrazones in particular is a most striking feature, and would probably cause surprise if the isomers were known to be structurally different, for example, in the sense that one represented a hydrazone and the other an azo-compound.

The spectra were photographed with the aid of a spectrograph made by Hilger, and kindly presented to the Chemical Department of this University by Mr. C. A. Schunck. The authors also desire to express their indebtedness to Professor E. C. C. Baly, who presented the plates used in calibrating the photographs, and offered many valuable suggestions.

Chemical Laboratories,
The University, Manchester.

CCIII.—*The Solubility of Cuprous Oxide in Aqueous Ammonia Solutions, and the Composition of the Cuprous-ammonia Complex.*

By Frederick George Donnan and John Smeath Thomas.

In the following paper an account is given of determinations of the solubility at 25° of crystalline cuprous oxide in aqueous ammonia solutions of varying strengths. The investigation was primarily undertaken in order to throw some light, if possible, on the composition of the cuprous-ammonia complexes existing in such solutions.

Preparation of Materials.

The cuprous oxide was prepared as follows. Equal weights of copper sulphate and sucrose were dissolved in water, and potassium hydroxide solution added until almost the whole of the precipitate had re-dissolved. This solution was kept at 70° until the cuprous oxide had separated out. Two batches of oxide were prepared in this way. In the first case the solution was large in bulk and relatively dilute, the cuprous oxide separating slowly and possessing a dark red colour, whilst in the second case, when the solution was much more concentrated, the precipitate formed in a shorter time, and was bright red. This second preparation proved to be slightly more soluble in ammonia solutions than the first. This is probably due to the fact that it consisted of smaller crystals.

In each case the oxide was collected by the aid of the pump, well washed with water, then with alcohol and ether, and dried in a vacuum desiccator over sulphuric acid. Analysis of these preparations gave: *Preparation I* (dark red), Cu = 88·62. *Preparation II* (bright red), Cu = 88·59. Cu_2O requires Cu = 88·68 per cent.

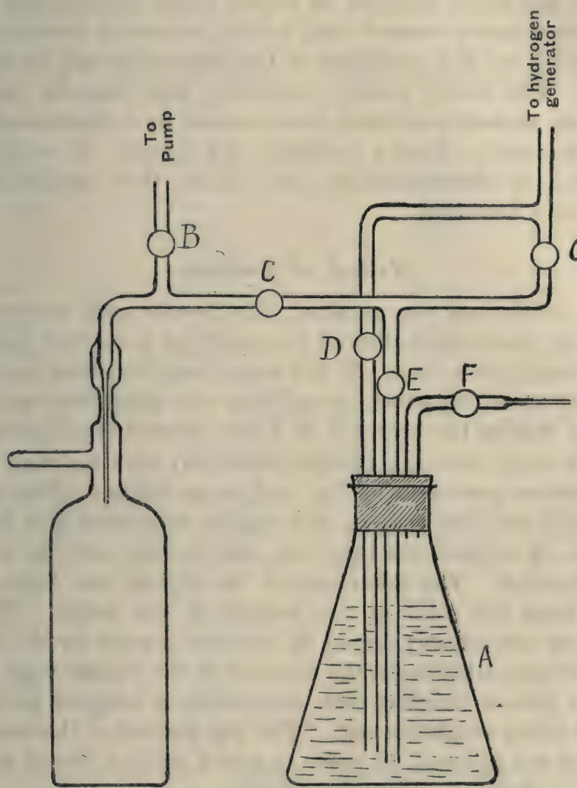
The stock ammonia solution was prepared by distilling ordinary "pure" concentrated ammonia solution over lime, the gas being passed into pure distilled water. The concentrated stock solution so prepared was carefully guarded from entrance of carbon dioxide, and was diluted as required.

Apparatus and Method.

The apparatus used for the solubility determinations is shown in the accompanying figure. It consists essentially of a narrow-necked bottle, with a device for introducing the ammonia solution and sealing in an atmosphere of hydrogen. The bottle has a long, narrow neck, which, after the solid has been introduced, is con-

stricted. A tube, one end of which has been drawn out to a capillary, is passed through the constriction and then sealed, first of all into the neck of the bottle (inside seal), and then to the rest of the apparatus.

The ammonia solution is contained in the flask A, and as a preliminary, air is removed from this and the flask by a stream of hydrogen which escapes through F. The process of filling the



bottle with ammonia solution was as follows. The bottle is first exhausted, and then filled with hydrogen by closing B and opening C and G. This was repeated several times to ensure the removal of all air, after which the bottle was finally exhausted. On now opening C, E, and D (keeping B, G, and F closed), the air-free ammonia solution is driven over by the pressure of the hydrogen into the bottle, the capillary delivery tube preventing any wetting of the constriction. As soon as sufficient solution has been driven over, E is closed, and the remaining space in the bottle filled with

hydrogen at nearly atmospheric pressure by opening G. Finally, all the taps are closed, the bottle immersed in ice (to reduce the ammonia pressure), and the constricted neck of the bottle sealed up without removing the inside capillary tube. It was found quite possible to do this, if the capillary tube was sufficiently thin. A little finely divided copper was generally added to the solid cuprous oxide to remove any trace of oxygen remaining in the bottle, and to reduce any small quantity of cupric oxide accidentally present. Special experiments showed that a small excess of metallic copper had no effect on the solubility of the cuprous oxide, as might be expected. The sealed bottles containing the cuprous oxide (in excess) and ammonia solution were rotated in a thermostat at 25° for periods varying from a fortnight to a month. A careful series of preliminary determinations had shown that equilibrium was attained in a fortnight.

Method of Analysis.

After equilibrium was attained, the bottles were removed from the rotating shaft, and allowed to remain in a vertical position in the thermostat for a week. If the experiment had been successfully carried out up to this point, the solution was quite clear and colourless. Any bottles the contents of which showed the slightest trace of a bluish tinge (indicating slight oxidation) were rejected.

The solution was removed for analysis as follows. The side-tube of the bottle was first opened, and rapidly connected to a hydrogen generator. The neck was then cut, and a cork carrying a pipette at once inserted. The lower end of the pipette was kept at least an inch from the solid at the bottom of the bottle. The clear solution was now quietly forced up into the pipette by the pressure of the hydrogen, whereupon the contents of the pipette were without delay run into a weighed flask containing a weighed amount (in excess) of dilute sulphuric acid. The top portion of the contents of the pipette was rejected, in order to guard against loss of ammonia during the process of filling the pipette.

The total ammonia was estimated by distilling over from excess of alkali in the usual way. In the remaining liquid the excess of alkali was neutralised by nitric acid, the solution then made considerably acid by more nitric acid, and the copper deposited electrolytically on a rotating platinum cathode (platinum crucible). The deposited copper was washed, dried, and weighed with the usual precautions.

Experimental Results.

In tables I and II are given the results of the solubility determinations at 25°, with the two preparations of cuprous oxide previously referred to.

TABLE I.

Preparation No. 1.

Concentration of total copper.		Concentration of total ammonia.	
Grams per 1000 grams of solution.	Mols. per 1000 grams of solution.	Grams per 1000 grams of solution.	Mols. per 1000 grams of solution.
0·3593	0·00566	3·91	0·23
0·5024	0·00791	12·07	0·71
0·6869	0·01080	13·77	0·81
0·6964	0·01095	16·15	0·95
1·0144	0·01597	27·03	1·59
1·0462	0·01645	32·64	1·92
1·0557	0·01660	36·89	2·17
1·2243	0·01924	45·73	2·69
1·3229	0·02081	68·68	4·04
1·4882	0·02340	74·12	4·36
1·5105	0·02375	81·26	4·78
1·6313	0·02565	98·52	5·56
1·6981	0·02670	122·40	7·20

TABLE II.

Preparation No. 2.

Concentration of total copper.		Concentration of total ammonia.	
Grams per 1000 grams of solution.	Mols. per 1000 grams of solution.	Grams per 1000 grams of solution.	Mols. per 1000. grams of solution.
0·4229	0·00665	7·82	0·46
0·6678	0·01050	8·16	0·48
0·9890	0·01555	22·61	1·33
1·0494	0·01650	28·39	1·67
1·3528	0·02127	54·15	3·19
1·5047	0·02366	72·08	4·24
1·5963	0·02510	78·20	4·60
1·6555	0·02603	102·05	6·00

A comparison of curves plotted from the results given in tables I and II shows that Preparation No. 2 is uniformly more soluble than Preparation No. 1. As stated before, this is probably due to the fact that No. 2 contains a much larger proportion of very small, micro-crystalline particles.

Formula of the Cuprous-Ammonia Complex.

Owing to the excessively small solubility of cuprous oxide in pure water, the solutions obtained in the foregoing experiments must contain practically only a complex cuprous-ammonia hydroxide, the formula of which we may represent as $(Cu\cdot nNH_3)OH$, and the

corresponding ions. The solution may in reality contain a number of different complex hydroxides, corresponding with different values of n, in which case the value of n obtained in the following calculation will represent an average value. We shall proceed, however, on the simplifying assumption that the solutions contain in the main only one type of complex, and endeavour to ascertain the corresponding value of n (compare Bonsdorff, *Zeitsch. anorg. Chem.*, 1904, **41**, 132). The condition of saturation with respect to solid, crystalline cuprous oxide leads to the equilibria:

$$Cu_2O + H_2O \rightleftarrows 2CuOH \rightleftarrows (2Cu^{\cdot} + 2OH').$$

For dilute solutions we may therefore write:

$$[Cu^{\cdot}] \times [OH'] = L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

where L is a constant.* It may be observed that this relation can only be an approximation, and perhaps a very rough approximation, for the stronger ammonia solutions, since, quite apart from the "physical" effect of the increasing ammonia concentration on the solubility of cuprous oxide, the quantity L involves the concentration of the water in the solution.

The dissociation of the complex ion $Cu^{\cdot}(NH_3)_n$ leads to the equilibrium:

$$Cu^{\cdot}(NH_3)_n \rightleftarrows Cu^{\cdot} + nNH_3.$$

The concentration of ammonia, as ammonium hydroxide and "free" ammonia, will be equal to $[NH_3] - n[Cu]$, where $[NH_3]$ = molar concentration of total ammonia, and $[Cu]$ = molar concentration of total copper.

In not too strong solutions, since $NH_3 + H_2O \rightleftarrows NH_4OH$, we may put the concentration of "free" ammonia as approximately proportional to $[NH_3] - n[Cu]$.

The dissociation-equilibrium of the complex cuprous-ammonia kation leads then to the equation:

$$[Cu^{\cdot}] \times \{[NH_3] - n[Cu]\}^n = k[Cu^{\cdot}(NH_3)_n] \quad . \quad . \quad . \quad (2).$$

Elimination of [Cu] between equations (1) and (2) leads to the equation:

$$\frac{[Cu^{\cdot}(NH_3)_n] \times [OH']}{\{[NH_3] - n[Cu]\}^n} = \frac{L}{k} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

As the copper will exist in the solution practically only as complex hydroxide, and as this, owing to its small concentration, may be regarded as nearly completely ionised, we may without great error write $[Cu^{\cdot}(NH_3)_n] = [Cu]$.

If, further, we neglect the concentration of OH'-ion due to

* In this equation and the following equations the square brackets indicate molar concentrations.

ionisation of ammonium hydroxide in comparison with that arising from the complex hydroxide, we may write also:

$$[OH'] = [Cu^{\cdot}(NH_3)_n] = [Cu].$$

It may be observed here that this last approximation requires justification (see later, p. 1795). With these approximations, equation (3) assumes the form:

$$\frac{[Cu]^2}{\{[NH_3] - n[Cu]\}^n} = \frac{L}{k} = \text{const.} \quad . \quad . \quad . \quad . \quad (4).$$

Since the analytical results give directly the values of [Cu] and [NH_3], equation (4) may be employed to determine the value of n. For example, if $n = 2$, then $\frac{[Cu]}{[NH_3] - 2[Cu]} = \text{constant}.$

If we put the concentration of free ammonia in the solution proportional to the partial pressure (p_{NH_3}) of ammonia in the vapour-phase in equilibrium with the solution, we can write (4) in the form:

$$\frac{[Cu]^2}{p^n_{NH_3}} = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

The values of p_{NH_3} were obtained from the results of Perman at 25° (Trans., 1901, **79**, 718; 1903, **83**, 1168), allowance being made in each case for the ammonia combined with the copper.

In the following table are shown the results as calculated from the solubility-data of table I. The values of [Cu] and [NH_3] have been read from a smooth curve drawn from these data.

TABLE III.

[Cu].	[NH_3].	$\frac{[Cu]^2}{[NH_3]-[Cu]}$ k_1.	$\frac{[Cu]^2}{p_{NH_3}}$ k_2.	$\frac{[Cu]^2}{\{[NH_3]-2[Cu]\}^2}$ k_3.
0·0050	0·28	91×10^{-6}	71×10^{-4}	185×10^{-4}
0·0090	0·60	137×10^{-6}	104×10^{-4}	157×10^{-4}
0·0130	1·20	142×10^{-6}	105×10^{-4}	111×10^{-4}
0·0170	2·04	138×10^{-6}	104×10^{-4}	85×10^{-4}
0 0210	3·36	132×10^{-6}	92×10^{-4}	63×10^{-4}

Although both k_1 and k_2 exhibit an undoubted maximum, the relative constancy of these values in comparison with the wide variation of k_3 points unmistakably to the value $n = 1$, and the formula ($Cu \cdot NH_3$)OH for the complex cuprous-ammonia hydroxide.

It may be remarked that the values given under [Cu] and [NH_3] are expressed in terms of mols. per 1000 grams of solution, and not in terms of mols. per litre. The varying density of the ammonia solutions will therefore to some extent affect the constancy of k_1 and k_2 (k_3 will clearly not be affected). As the variation in density of the ammonia solution does not amount to more than two or three per cent., this source of error may be neglected for the

purposes of the present calculation. In order to obviate any objection, the following table shows the values of $\frac{[Cu]^2}{[NH_3]-[Cu]}$, where both [Cu] and $[NH_3]$ are expressed as fractional molar concentrations; for example:

$$[Cu] = \frac{\text{Mols. copper}}{\text{Mols. copper + mols. ammonia + mols. water}}.$$

TABLE IV.

Values of k_1 for fractional molar concentrations.

$16{\cdot}3 \times 10^{-7}$
$24{\cdot}7 \times 10^{-7}$
$25{\cdot}8 \times 10^{-7}$
$25{\cdot}1 \times 10^{-7}$
$21{\cdot}5 \times 10^{-7}$

These values correspond in order with the values given in table III, and exhibit a similar maximum.

As shown in table II, the second preparation of cuprous oxide showed uniformly higher solubilities in ammonia solution than the first preparation. The following table (V) shows the values of k_1 as calculated from the solubility data given in table II. The values of [Cu] and $[NH_3]$ have been, as in the previous case, read from a smooth curve drawn through the experimental points.

TABLE V.

[Cu].	$[NH_3]$.	$\frac{[Cu]^2}{[NH_3]-[Cu]}$.
0·005	0·220	116×10^{-6}
0·009	0·505	163×10^{-6}
0·0130	0·970	176×10^{-6}
0·0170	1·710	171×10^{-6}
0·0210	2·990	149×10^{-6}

As pointed out previously, in arriving at the equation whereby the values of the "constants" have been calculated, the ionisation of ammonium hydroxide in presence of the highly dissociated cuprous-ammonia hydroxide was neglected. How far such an approximation is justifiable may be seen from the following considerations.

Let c = molar concentration of total ammonia.
pc = molar concentration of total copper.

Assuming the copper all present in the solution as $Cu(NH_3)OH$, and this as practically completely ionised, the hydroxyl ion concen-

tration corresponding therewith will be pc. If α = degree of ionisation, and k = ionisation constant of ammonium hydroxide,* then:

$$k(1-p)(1-\alpha)c = (1-p)\alpha c \times \{(1-p)\alpha + p\}c,$$

or,

$$k(1-\alpha) = \alpha c\{(1-p)\alpha + p\}.$$

In this equation p and c are known from the analytical data, and the values of k can be obtained from the data of Goldschmidt (*Zeitsch. anorg. Chem.*, 1901, **28**, 122). Hence, α can be calculated, and so the values of $(1-p)\alpha c$ (hydroxyl ion concentration due to ammonia) determined and compared with the values of pc (hydroxyl ion concentration due to cuprous ammonia hydroxide). The results of this calculation are shown in the following table.

TABLE VI.

$[NH_3]$.	[Cu].	[OH′] in pure ammonia solution.	[OH′] due to ammonia in cuprous ammonia solution.	[OH′] due to cuprous ammonia hydroxide.
0·28	0·0050	0·0098	0·00093	0·0050
0·60	0 0090	0·0072	0·0011	0·0090
1·20	0·0130	0·0048	0·0013	0·0130
2·04	0·017	0·0036	0·0013	0·0170

Table VI shows that in the solutions investigated the hydroxyl ion concentration arising from the ionisation of the uncombined ammonia is, in the stronger ammonia solutions, sufficiently small in comparison with that due to the ionisation of the cuprous ammonia hydroxide (assumed practically completely ionised). The approximation introduced into the main calculation (see p. 1793) is therefore justified in the case of not too dilute solutions of ammonia, as the following table shows.

TABLE VII.

[Cu].	$[NH_3]$.	$k_1 = \dfrac{[Cu].[OH']}{[NH_3]-[Cu]}$.
0·005	0·28	108×10^{-6}
0·009	0·60	154×10^{-6}
0·013	1·20	156×10^{-6}
0·017	2·04	154×10^{-6}

In the above table [OH′] = molar concentration of total hydroxyl ion, as calculated from the results given in table VI.

These considerations suffice to explain the rise of the "constant" in the more dilute solutions of ammonia. The fall observed in the stronger ammonia solutions is almost certainly to be ascribed to the "salting-out" effect of the ammonia, and the decrease in the concentration of the water, both of which will tend to diminish the

* α is really the "apparent" degree of ionisation, and k the "pseudo" ionisation constant, of the total uncombined ammonia.

quantity L, the "solubility-product" of the cuprous oxide (compare p. 1792). Dawson, in his investigation of the solubility of crystalline cupric hydroxide in aqueous ammonia solutions (*Zeitsch. physikal. Chem.*, 1909, **69**, 114), has observed a similar variation of the analogous "constant" (where, however, $n=4$). Our explanation of the variation is substantially the same as that given by Dawson, with whom we entirely agree.

It is curious that we find the formula $(Cu^{I}\cdot NH_3)OH$ for the complex cuprous ammonia hydroxide, whereas Dawson's results are best explained by the formula $(Cu^{II}\cdot 4NH_3)(OH)_2$. Bonsdorff (*loc. cit.*) deduced from his work on the solubility of cupric hydroxide in ammonia solution the formula $(Cu^{II}\cdot 2NH_3)(OH)_2$, but Dawson has conclusively demonstrated the erroneous nature of this result; thus, when the copper atom changes as regards its primary positive valency from the univalent to the bivalent state, its secondary or residual valency, that is, combining capacity, for ammonia increases in a greater proportion. The composition of many complex cuprous and cupric compounds (containing a complex copper cation) supports this conclusion (compare Abegg's *Handbuch der anorg. Chem.*, II, 1, p. 536).

THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,
THE UNIVERSITY OF LIVERPOOL.

CCIV.—*The Synthesis of Hydrocarbons at High Temperatures.*

By JOHN NORMAN PRING and DORIAN MACEFIELD FAIRLIE.

IN a previous investigation by one of us (Trans., 1910, **97**, 489) the synthesis of methane was investigated between the temperatures 1200° and 1500°. The yield of methane diminished somewhat with progressive use of the same carbon, but finally attained a constant value. This decrease in the methane formation was probably due to graphitisation of the carbon, the minimum values being obtained from the first when graphite was used.

The formation of ethylene was observed at 1800° and at higher temperatures. In experiments carried out at 1200—1500°, the final quantity of methane obtained appeared to be increased by using platinum as a catalyst in contact with the carbon. No satisfactory explanation could be given of this, nor of the fact that the amount of methane, which, of course, diminishes with the temperature,

began to increase at 1550°, although the formation of acetylene could not be detected below about 1800°.

The points which still remain to be cleared up are whether the quantities of methane obtained in these earlier experiments between 1200° and 1500° are the true equilibrium values, or is the yield affected by the intermediate formation of traces of acetylene or some other hydrocarbon which it has not yet been found possible to detect, or is it affected by any other cause.

Gautier and Clausmann (*Compt. rend.*, 1910, **151**, 355) have shown that by the action of oxides of iron on mixtures of carbon monoxide and dioxide at 1250°, an amount of methane is formed which is equal to 0·20 per cent. of the hydrogen present. This is probably a rough measure of the equilibrium value, but the conditions of the experiment were not sufficiently precise for an exact evaluation.

In order to elucidate the remaining points of uncertainty, the following series of experiments were carried out in the present research.

Part I.—The influence of different catalysts on the final quantity of methane obtained.

Part II.—The surrounding of the heated carbon rod by an electric field of high potential in order to influence any ionisation effect from the heated carbon.

Part III.—The detection of any hydrocarbons formed in very small quantity, or as intermediate compounds, by rapid continuous circulation of the gas through the apparatus, and then through charcoal, cooled by liquid air, in order to condense and retain any hydrocarbons as soon as possible after their formation.

Part IV.—Measurements were made of the rate at which acetylene and ethylene react with hydrogen at different temperatures, and the nature of the products obtained was ascertained.

Part I.—Effect of Catalysts.

The form of apparatus used was the same as that described in the earlier work (Trans., 1910, **97**, 500). The hydrogen was purified by filtering through a palladium tube (*loc. cit.*, p. 502). The only part of the apparatus to be subjected to a high temperature was the carbon. Temperature readings were made, as before, by means of the Wanner optical pyrometer, which was first carefully calibrated.

Analysis of Gas.—In the samples in which acetylene was absent, the gas was withdrawn from the apparatus, stored over glycerol and water, and analysed by taking from 1000 to 1500 c.c. and

removing the excess of hydrogen with palladium foil, until the volume was reduced to 35—50 c.c.

After removal of the carbon monoxide, a fractional combustion of the hydrogen was brought about by mixing the gas with an excess of oxygen, and passing through a U-tube containing palladium black, and maintained at 80—100° in a small water-bath (compare Hempel, *Gas Analysis*, 1906, p. 178). After complete removal of the hydrogen in this way, the remaining mixture was ignited by a spark, and the contraction measured. The carbon dioxide formed was then removed by potassium hydroxide. By noticing the ratio between the contraction after ignition and the carbon dioxide formed, the saturated hydrocarbon was always identified as methane, for which the above ratio was always found to be 2 : 1 (with ethane this would be $2\frac{1}{2}:2$, and with propane 1 : 1).

For a satisfactory analysis of the gases obtained in experiments where unsaturated hydrocarbons were present, it was found necessary to make an examination of the methods available for the separation of acetylene and ethylene.

Use of Ammoniacal Silver Nitrate.—By taking a mixture of acetylene and hydrogen it was found that, provided the reagent was fresh, the whole of the former was absorbed by a concentrated solution of ammoniacal silver nitrate, after shaking for three minutes.

35·5 C.c. of pure ethylene were shaken with the same reagent. The absorption after three minutes amounted to 7·63 c.c., and after another three minutes' treatment a further 2·5 c.c. was absorbed.

Bromine water containing an excess of bromine was found completely to absorb acetylene and ethylene, if shaken, after three minutes. No means of absorbing acetylene without affecting the ethylene was found. Ammoniacal silver nitrate was used, with which the absorption of the acetylene was complete, and that of the ethylene assumed to amount to one-quarter to one-fifth of the total quantity present. The remainder of the ethylene was absorbed by treating the gas with bromine water, followed by potassium hydroxide solution. The hydrogen and methane were then estimated as described above.

Purification of Carbon.—The carbon, in the form of a rod, usually 4 mm. in diameter and about 8 cm. long, was purified by heating in chlorine to about 1400° for one to two hours in a vessel similar to the reaction vessel, but in which the brass water-cooled holders were previously coated with shellac. This form of apparatus is specially suited for this purification, as the chlorides formed from the impurities distil rapidly away, and condense in the cold parts of the apparatus. The vessel was always evacuated, and refilled with

chlorine several times while the heating was continued. The carbon was then heated in hydrogen in the same manner for the same time, the apparatus being frequently exhausted to a low pressure. After transferring to the reaction vessel (*loc. cit.*, p. 501), the carbon was heated for two to three hours, to about 1200°, at the low pressure of about 0·01 mm. In this way, the ash content of the carbon was usually reduced to below 0·1 per cent., and the hydrogen below 0·01 per cent. In the case of the carbon rods which were used in presence of platinum or palladium as a catalyst, these metals, to the amount of about 0·2 gram, were coated on the carbon, by electrodeposition, after the treatment in chlorine. The order of the experiments has been carefully noted in the results below to show in some cases the effect of continued use of the same carbon.

Use of Platinum as a Catalyst.

Carbon coated with Platinum. 4 mm. × 11 cm.

Order of experiment.	Duration.	Temp. (approx.)*	Product. CO. Per cent.	Product. CH_4. Per cent.
1.	$1\frac{3}{4}$ hrs.	1250°	0·09	0·522
2.	$3\frac{1}{2}$,,	1150	0·11	0·702

Carbon coated with Palladium. No. 1. 5 mm. × 11·2 cm.

Order of experiment.	Duration.	Temp. (approx.)*	CO.	CH_4.
1.	$1\frac{1}{4}$ hrs.	1175°	0·08	0·630
2.	$\frac{1}{2}$ hr.	1400	0·22	0·328

Carbon coated with Palladium. No. 2. 5 mm. × 5·5 cm.

Order of experiment.	Duration.	Temp. (approx.)*	CO.	CH_4.
1.	$1\frac{1}{4}$ hrs.	1320°	0·08	0·498
2.	3 ,,	1450	0·56	0·212

Carbon coated with Silicon.—The rod (5 mm. × 9 cm.) was coated with an even deposit of silicon by heating in an atmosphere of hydrogen and silicon tetrachloride, at about 1700°, for twenty minutes under conditions which have been determined by one of us, in conjunction with W. Fielding (Trans., 1909, **95**, 1497).

Order of experiment.	Duration.	Temp. (approx.)*	Product. CO. Per cent.	CH_4.	C_2H_2.	C_2H_4.
1.	$1\frac{1}{4}$ hrs.	1225°	0·004	0·218	—	—
2.	1 hr.	1600	0·56	0·286	0·0016†	—
3.	35 mins.	1710	0·02	0·467	0·95	?

The above results show that there is no appreciable difference between platinum and palladium in their influence as catalysts in assisting the reaction, and that silicon has no appreciable catalytic effect. The results obtained with platinum are in complete agreement with those found in the earlier work (*loc. cit.*, p. 510).

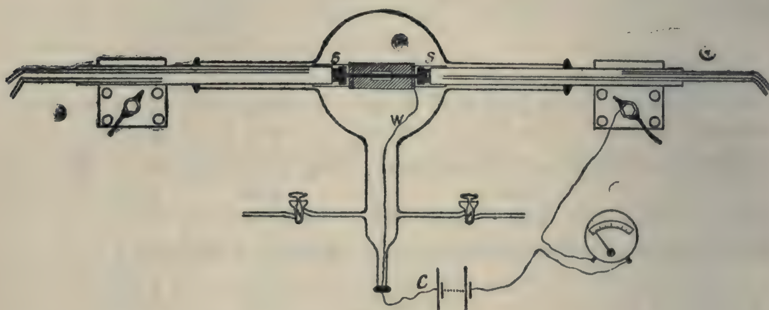
* Not corrected for departure from "black body" radiation from the coated surface.

† Estimated colorimetrically.

Part II.—Influence of an Electric Field Surrounding the Heated Carbon.

At the suggestion of Mr. R. E. Slade, a number of experiments were carried out to ascertain if any influence is exerted by ionisation from the carbon on the formation of methane. A cylinder of fine platinum gauze, 8 cm. long and 2 cm. in diameter, was taken (Fig. 1). A rectangular opening in the middle 1 cm. × 0·6 cm. was made to allow an uninterrupted view of the rod by the pyrometer. Thin tubes of fused silica were inserted at *S S* to prevent contact of the platinum with the brass tubes. A wire at *W* enabled electrical contact to be made with the cylinder *S*. The whole of this was then mounted in the reaction vessel by sliding through the side-tubes, and the wire *W* allowed to emerge through

FIG. 1.



the neck at the bottom, where an air-tight joint was made by means of wax. In this way, a difference of potential could be applied between the heated rod and the surrounding cylinder by means of a circuit *C*, which is independent of the one used for heating the rod. A difference of potential of from 200 to 400 volts in either direction could thus be maintained, and the ionisation current measured by using a milliammeter in the circuit.

With a carbon rod 9 cm. long and 5 mm. in diameter, heated in an atmosphere of hydrogen, the following values were found for the ionisation current:

	Ionisation current when field on gauze was	
Temp.	+200 to 300 milliamps.	−200 to −300 milliamps.
1200°	0·02	—
1550	0·88	0·07
1625	1·20	0·08
1720	—	0·11
1845	5·0	—

The current produced when the platinum was negatively charged must have arisen from the negative ionisation of this metal, which became heated by radiation from the carbon, as subsequent work on the ionisation from carbon at high temperatures has shown that no measurable amount of positive ions are produced at any temperature below 2000°.

Rod No. 1.—Amorphous carbon, 9 cm. × 5 mm., purified as described above (p. 1800.)

Order of experiment.	Duration.	Temp.	Charge on platinum cylinder.	Product. CO.	CH_4.	C_2H_2.	C_2H_4.
				Per cent.			
1.	3 hrs.	1330°	+210	0·5	0·212	—	—
2.	2½ ,,	1330	−375	0·14	0·200	—	—
3.	1 hr.	1560	+360	0·62	0·260	—	—

Rod No. 2.—Partly purified by heating in a high vacuum for three hours at 1200°.

1.	8 mins.	1850°	+210	1·6	1·46	0·43	0·90

The rod was afterwards analysed, and found to contain 0·32 per cent. of ash.

Rod No. 3.—Partly purified by heating electrically in chlorine for fifteen minutes at about 1200°, and then in hydrogen, and, after mounting in reaction vessel, heating in a high vacuum for four hours to about 1200°.

1.	12 mins.	1850°	−200	2·5	1·01	0·60	0·50

Rod No. 4.—Not purified. 5 mm. × 8 cm.

1.	12 mins.	1850°	+210	2·1	0·57	0·40	0·32

Rod No. 5.—Not purified. 4 mm. × 8 cm.

1.	7½ mins.	1825°	−220	5·0	0·69	0·50	?

Rod No. 6.—4 mm. × 7 cm. Purified by heating in chlorine for fifteen minutes, then in hydrogen for the same time, and finally in a vacuum for an hour.

1.	5 mins.	1900°	+220	4·2	0·50	1·05	?

Rod No. 7.—5 mm. × 7 cm. Purified by heating electrically in hydrogen at 1600—1700° for three hours with occasional exhaustions.

Order of experiment.	Duration.	Temp.	Charge on platinum cylinder.	Product. CO.	CH_4.	C_2H_2.	C_2H_4.
				Per cent.			
1.	30 mins.	1560°	−200	0·24	0·243	—	—
2.	30 ,,	1680	−200	0·50	?	trace (0·001%)	?
3.	30 ,,	1650	+200	0·05	0·220	trace (0·001%)	?
4.	30 ,,	1550	+200	<0·005	0·180	—	?
5.	30 ,,	1580	−190	<0·003	0·182	—	?
6.	70 ,,	1525	−195	<0·003	0·180	—	?
7.	3¼ hrs.	1215	−220	<0·003	0·188	—	—
8.	3 ,,	1230	+340	0·01	0·201	—	—

At the end of this series the carbon rod was analysed, and found to contain 0·05 per cent. of ash.

The formation of acetylene at 1650° and 1680° was detected by passing a large quantity of the gas through a small washing spiral containing ammoniacal cuprous chloride, by which method the presence of 0·001 per cent. of acetylene can be shown. In this way it was possible to detect the acetylene formed at a temperature about 100° below that previously found.

The above experiments, in which long-continued use was made of the same carbon, show clearly that ionisation by the carbon makes no difference to the yield of methane. The quantity of methane obtained at 1525—1550°, namely, 0·180 per cent., is in agreement with the results obtained in earlier work (Trans., 1910, **97**, 510).

At the lower temperatures, 1215—1330°, where the reaction has been found to be so slow, sufficient time was not allowed for the formation of methane to reach its maximum value, but the above experiments prove that the ionisation of carbon has no effect on the rate at which methane is formed.

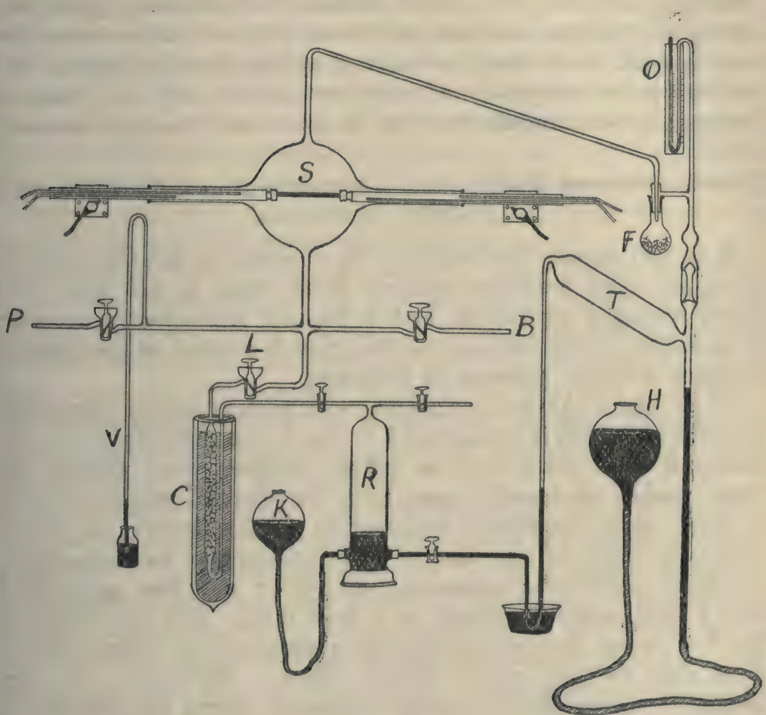
Part III.—Detection of Hydrocarbons formed as Intermediate Compounds, or in very small quantities, by continuously circulating the gas through the reaction vessel at different pressures, and then at atmospheric pressure through charcoal at −180°.

The reaction vessel was similar to the one previously used, but of smaller capacity. The globe *S* (Fig. 2) was 13 cm., and the side-tubes 1·3 cm. in diameter. The water-cooled brass tubes fitting into these were 1 cm. in diameter. Graphite plugs were inserted in the sealed brass tubes as usual, and an amorphous carbon rod of 3 or 4 mm. diameter and 7 to 8 cm. long was fitted.

The pressure of gas inside the apparatus was indicated by the mercury gauge *V* and the vacuum gauge *O*. The vessel was exhausted to a fraction of a millimetre by means of a Sprengel automatic mercury pump connected to *P*. The vessel was filled with pure hydrogen, which entered at *B*, after passing through a

heated palladium tube. The large Töpler pump T, fitted with a drying bulb F, enabled gas to be quickly removed from the reaction vessel at any pressure, and passed into the reservoir R, where, by regulating the height of the mercury K, the pressure was usually adjusted to be a little above atmospheric. By then turning and carefully regulating the tap L, the hydrogen could be slowly re-admitted into the reaction vessel, after passing through the tube C containing cocoanut charcoal, which was kept immersed in liquid air. It was, of course, first necessary to saturate the charcoal with

FIG. 2.



hydrogen, a large quantity of which is absorbed at atmospheric pressure. A very rapid circulation of gas and removal of absorbable constituents could thus be carried out at different gaseous pressures in S. However, since this absorption is probably not complete, the method cannot be applied for precise quantitative results.

In many of the experiments, the operation of the Töpler pump was made mechanical by the use of a motor and pulley for raising and lowering the reservoir H. In this way a steady and known rate of circulation could be kept up for several hours.

Fractional Separation of Hydrocarbons by Absorption with Charcoal at Low Temperatures.

It was found that if methane and acetylene, together with a large excess of hydrogen, are absorbed in charcoal cooled by liquid air (−190° to −180°), and if the liquid air is then replaced by a mixture of ether and carbon dioxide (−80°) and the gas withdrawn from the charcoal until the pressure is reduced to 3 mm., then nearly all the hydrogen is given off, about one-third of the methane (b. p. −160°), and only a trace of the acetylene (b. p. −85°). On removing the ether and carbon dioxide, the remaining gases, consisting of hydrogen, methane, acetylene, ethylene, carbon monoxide, and dioxide, could then be removed by the Sprengel pump. The last traces of acetylene and ethylene could only be removed, however, by warming the charcoal for some time in a high vacuum.

Reaction between Unsaturated Hydrocarbons and Hydrogen when Absorbed in Charcoal.

It is well known that charcoal, by condensing, has the power of bringing about reactions between gases which do not take place under ordinary conditions, and it became consequently necessary to ascertain if any influence of this kind is exerted on acetylene or ethylene when in presence of hydrogen.

In the use of charcoal for dealing with gaseous carbon compounds, an obstacle which is encountered is due to the difficulty of entirely removing such compounds as carbon dioxide, water vapour, and other readily condensable gases from the charcoal, small quantities of such gases constantly reappearing during future use of the charcoal. The charcoal used in these experiments was prepared by carefully carbonising cocoanut shell, which was then granulated, and a small quantity placed in a glass tube. This was exhausted for four or five days with a Sprengel pump, and the charcoal heated from time to time with a Bunsen flame. Hydrogen was then admitted several times, in some cases after cooling the charcoal by liquid air, and then pumped off until a high vacuum was obtained. After treating in this manner, some hydrogen was admitted, withdrawn after warming the charcoal, and, on analysis, still found to contain 1 c.c. of carbon dioxide.

A number of experiments were carried out, in which mixtures of acetylene or ethylene and hydrogen were left in contact with cocoanut charcoal at different temperatures. The reaction between these unsaturated hydrocarbons and oxygen was investigated in a similar manner. The results showed that the reaction between acetylene and hydrogen, when occluded in charcoal and heated at

100—200°, leads to the formation of ethylene in quantities not exceeding about 2 per cent., and an amount of methane which is smaller than this.

In presence of oxygen, acetylene and ethylene are partly oxidised at about 200°, but only slightly, if at all, at room temperatures. Exact measurements of the amount of carbon dioxide present when only in small quantities was prevented by the difficulty of completely removing this gas from the charcoal after each experiment. The results show that carefully purified cocoanut charcoal can, without appreciable error, be used for the fractional separation of hydrocarbons in presence of hydrogen.

After these preliminary experiments, use was made of the circulation apparatus described above, and shown in Fig. 2. If the intermediate formation of acetylene or any other stable hydrocarbon takes any part in the yield of methane, then by continuously circulating the gases through the reaction vessel and through the cold charcoal tube, any such compounds will be partly or entirely condensed, and after a sufficient quantity has collected, can be removed and analysed in the usual manner.

Experiments were, in this way, carried out at various pressures. If acetylene plays any part in the reaction, it follows that by working at a lower pressure the ratio of the less condensed molecule acetylene to the more condensed methane will be higher than at a higher pressure. The pressure of gas in the reservoir *R* (Fig. 2) and in the charcoal was usually higher than atmospheric, to enable more efficient condensation, and to obviate leaks through the rubber stoppers at the base of the reservoir.

Purification of Charcoal.—In order to remove the last traces of acetylene from the freshly prepared charcoal, it was found necessary to exhaust to the lowest possible pressure for a period of several days, occasionally heating and admitting hydrogen. It is probably not at all possible to remove all the water vapour and denser hydrocarbons. After the purification treatment, none of the latter were evolved, however, with the gases during subsequent experiments, so that their presence did not interfere with the measurements.

In the experiments of this series, very particular precautions were taken to obtain the carbon in the purest condition. In addition to the usual preliminary purification, only carbon was taken which had been used for a long interval in previous experiments, where it had undergone prolonged heating in hydrogen.

The experiment below is described in some detail, as it is typical of the remainder in this series.

Expt. 1.—The carbon rod (7 cm. × 4 mm.), which had been coated with platinum, was heated for five and a-half hours at 1400° in

hydrogen at a pressure of 12 to 14 cm. The pressure of gas in the mercury reservoir (R) was kept at 74 cm. (in all subsequent experiments this was kept at 77 cm.). The speed of circulation of the gas was arranged so that the volume in the vessel was renewed every two minutes. The total volume of gas circulated through the charcoal and measured at N.T.P. was estimated at 38 litres. A quantity of hydrogen was then removed from the charcoal while still at $-180°$, until the pressure was reduced to 2 cm. The liquid air around the charcoal was then replaced by ether and carbon dioxide at $-80°$, and 720 c.c. of gas removed, which reduced the pressure to about 1 cm. Most of the hydrogen was removed from this gas by condensing with palladium foil, and the residue found to contain 6·23 c.c. of methane and 2·10 c.c. of carbon monoxide. After warming the tube to room temperature, 22·5 c.c. more gas were withdrawn (the last portions being obtained by warming to about 200°). This last sample was found to contain 1·15 c.c. of ethylene, 0·72 c.c. of carbon monoxide, and 3·95 c.c. of methane, and no other hydrocarbon. The total gas condensed therefore contained:

CH_4, 10·18 c.c., or 0·026 per cent. of whole.
C_2H_4, 1·15 c.c., ,, 0·003 ,, ,,
CO, 2·85 c.c., ,, 0·007 ,, ,,

The experiments in this series can be represented in tabular form as follows:

No. of experiment.	Temp. of carbon.	Pressure of gas (cm.).	Duration of experiment.	Total volume of gas circulated (litres N.T.P.).	Percentage composition of gas. CH_4.	C_2H_4.	C_2H_2.	CO.
4.	1200°	7—30	4 hrs.	26	0·049	0·0005	nil.	0·01
2.	1225	50—60	10½ ,,	80	0·010	0·00014	nil.	0·04
1.	1400	12—14	5½ ,,	38	0·026	0·003	nil.	—
3.	1400	10—25	9 ,,	31	0·039	0·002	nil.	—
5.	1650	7—30	1½ ,,	10	0·1104	0·0025	0·012	—
6.	1800	76	7 mins.	2·5	—	0·052	0·024	0·11

Experiments 2 and 6 were conducted with pure carbon, and the others with platinum coated rods. In Nos. 3 to 5, the same carbon rod was used.

Blank Experiments.—Experiments were made to ascertain the extent to which impurities in any part of the apparatus, such as vapours from tap grease or wax, might have contributed to the hydrocarbon formation in any of the present work. For this purpose, use was made of a platinum strip, instead of carbon, and a complete experiment carried through, as in part III above, and another as in part I. It was found in both cases that the amount of methane was less than 5 per cent. of that obtained when using carbon under the same conditions.

Part IV.—Rate of Reaction of Acetylene and Ethylene with Hydrogen, and rate of Decomposition of Methane at various temperatures.

In the present work, which extends some preliminary measurements already made by one of us (Trans., 1910, **97**, 508), a simple means was devised to follow continuously the course of the reaction between acetylene and hydrogen, and the measurements were extended to the reaction between ethylene and hydrogen. The rate of decomposition of the methane formed into carbon and hydrogen could also be observed.

Apparatus.—A porcelain tube of 2 cm. internal diameter and 60 cm. long was arranged inside an electrical wire resistance furnace, so that the tube could be heated to any temperature up to 1200°, which could be read by means of a thermocouple placed alongside. The tube was provided with a manometer, and gases could be introduced at one end and removed at the other by means of a Töpler pump, whereby the tube could be exhausted.

A mixture of the hydrocarbon and hydrogen could be admitted, and in virtue of the volume change, the reaction could be followed by the change of pressure indicated by the manometer. Accurate measurements could thus be made of the relative rates of the formation of methane from hydrogen and acetylene, or ethylene, and of its decomposition; thus, in the case of acetylene and hydrogen reacting according to the equation $C_2H_2 + 3H_2 = 2CH_4$, or

$$C_2H_2 + H_2 = C + CH_4,$$

the methane formed is, in either case, equal to the contraction. When all this methane is decomposed, the volume will again assume its original value. It was found that this second change, the decomposition of methane, was very slow compared with the first, so that the first could be measured independently of the second without appreciable error.

The acetylene used was prepared from calcium carbide, and, after washing through concentrated potassium hydroxide solution, was liquefied by liquid air, redistilled, and then collected over a heavy oil in a gas-holder. A sample of the gas was analysed, and found to contain 95·5 per cent. of acetylene. This and another holder filled with hydrogen were placed in connexion with the porcelain tube, and, after exhausting, either gas could be admitted to the heated tube and the volume ascertained by reading the manometer.

The temperature of the tube was kept constant to within about 10° throughout the experiment.

The pressure at first was always atmospheric, and the course of the reaction could be followed by the rise of mercury in the mano-

meter. After a definite period, the remaining gas was removed and submitted to analysis.

Expt. 1.—Temperature 720°. $C_2H_2=21$; $H_2=79$.*

Time (mins.)	0	5	8	13	16	18	21
Pressure (mm.)	760	717	702	686	677	672	668

Final composition of gas, $C_2H_2=9{\cdot}5$; $C_2H_4=2{\cdot}0$; $CH_4=10{\cdot}0$. Contraction = 12 per cent.

Expt. 2.—Temperature 980°. $C_2H_2=26{\cdot}7$; $H_2=73{\cdot}3$.

Time (mins.)	0	1	2	3	6	17	28	36	40
Pressure (mm.) ...	760	733	725	718	703	682	682	683	683·5

Final composition of gas, $C_2H_2=3{\cdot}08$; $C_2H_4=0{\cdot}56$; $CH_4=11{\cdot}9$; $CO=2{\cdot}9$. Contraction = 10·1 per cent.

Expt. 3.—Temperature 745°. $C_2H_2=24{\cdot}8$; $H_2=75{\cdot}2$.

Time (mins.)	0	1	3	6	10	16	25	40	143	183	188	283
Pressure (mm.) ...	760	747	730	714	697	680	662	648	612	610	610	607

Final composition, $C_2H_2=1{\cdot}91$; $C_2H_4=1{\cdot}0$; $CH_4=16{\cdot}9$; $CO=0{\cdot}8$. Contraction = 20 per cent.

No other hydrocarbons but the above were found in any of these experiments.

Reaction between Ethylene and Hydrogen.—This was investigated in the same manner as above.

The ethylene used for this purpose was of 98 per cent. purity.

Expt. 1.—Temperature 860°. $C_2H_4=32$; $H_2=68$.

Time (min.)	0	2	3	4	8	12	18	28	32	40
Pressure (mm.) ...	760	742	739	735	722	711	707	703	702	702

Final composition, C_2H_2, *nil*; $C_2H_4=8{\cdot}5$; $CH_4=8{\cdot}3$; $CO=4{\cdot}5$. Contraction = 7·6 per cent.

Expt. 2.—Temperature 1000°. $C_2H_4=32$; $H_2=68$.

Time (mins.)	0	3	10	20	30	40	50	60	70	80	90	100	110
Pressure (mm.)	760	733	714	710	711	714	715	716	718	718	719	720	721

Final composition, C_2H_2, *nil*; $C_2H_4=3{\cdot}5$; $CH_4=12{\cdot}3$; $CO=3{\cdot}6$. Contraction = 5·5 per cent.

These results show that at temperatures between 700° and 900° acetylene reacts with hydrogen to give methane and ethylene. The amount of methane formed, as ascertained by analysis, was found

* The composition of the gases is given in percentages.

to correspond approximately with the contraction, as would follow from either of the reactions below:

$$(a)\ C_2H_2 + H_2 = CH_4 + C,$$
$$(b)\ C_2H_2 + 3H_2 = 2CH_4.$$

The amount of methane formed, however, was always considerably less than the loss of acetylene. This loss could not have arisen from the decomposition of the methane at first formed, as this reaction was found to be extremely slow, even when large quantities of methane were present. Consequently, even assuming all the methane to have been formed according to equation (*a*), some of the acetylene must have undergone decomposition according to the equation $C_2H_2 = 2C + H_2$, and a similar decomposition with the ethylene (compare Bone and Coward, Trans., 1908, **93**, 1197).

It is also seen from these results that, in the form of apparatus used, in which about one-half of the total volume of gas was heated to the particular temperature, the decomposition of acetylene in presence of hydrogen into methane and into carbon and hydrogen takes place at 720° to the extent of one-half in about twenty minutes. At 980° seven-eighths is similarly decomposed in forty minutes. The reaction between ethylene and hydrogen also takes place at about the same rate. The decomposition of methane into carbon and hydrogen, on the other hand, was too slow to be measured.

It follows from these measurements that in the experiments made on the synthesis of hydrocarbons by the circulation method (p. 1802) at temperatures below 1200—1300°, the acetylene or ethylene would be separated largely as such. Sufficient time had not been allowed for the formation of the quantities of methane obtained from the observed amounts of ethylene and acetylene. Consequently, most of the methane which was formed in these cases, and which was always largely in excess of the other hydrocarbons, must have arisen directly from the elements, or else through the intermediate formation of some hydrocarbon at present unknown.

At the higher temperatures of 1500° and upwards, the ethylene present would certainly account for most of the methane observed.

These results further show that the presence of ethylene will play a very large part in those experiments in which hydrogen was left in contact with the heated carbon over a long interval, even at 1200° (parts I and II). The amount of methane, on account of its comparatively great stability, would be raised above the equilibrium quantity at the temperature of the rod, on account of the polymerisation of the traces of ethylene formed with hydrogen in the cooler parts of the vessel.

The formation of methane from acetylene and hydrogen as con-

ducted with the heated porcelain tube is an interesting example of an intermediate product arising in quantities much larger than are permanently stable at the particular temperatures used.

The above work, which has demonstrated the synthesis of methane and also of ethylene at temperatures from 1200° upwards, still leaves undecided the question of the equilibrium between methane and hydrogen, and shows that this cannot be ascertained in the form of apparatus hitherto used.

Berthelot, using a method in which the whole of the reacting substances were at a uniform temperature, could detect no hydrocarbons at 1200—1300°, but the porosity of the vessel probably led to their oxidation.

Summary of Results and Conclusions.

The reaction between carbon and hydrogen has been investigated by quickly removing the products from the neighbourhood of the heated carbon, and circulating the gas in large quantities through charcoal cooled by liquid air. Any traces of hydrocarbons were thus retained in the charcoal by condensation, and afterwards analysed. At a temperature of 1200°, and at pressures from 10 to 60 cm., carbon was found to combine with hydrogen to give methane and ethylene, the rate of formation of the latter being about 1/100th that of the methane. The amount of acetylene formed at this temperature is very much less, and could not be detected.

Measurements which were made of the rate at which acetylene and ethylene react with hydrogen to give methane, show that the amount of the latter hydrocarbon formed in these circulation experiments could not all be attributed to the initial formation of ethylene. At higher temperatures the ratio of ethylene to methane increased, at 1400° the amounts found being in the proportion of 1 to 10. In this case the amount of methane formed from ethylene would, of course, be much greater than at 1200°.

At 1650° methane, ethylene, and acetylene are obtained, and, as at higher temperatures, the quantity of ethylene formed is about twice that of the acetylene.

Palladium in contact with the carbon was found to assist catalytically the formation of methane to the same degree as platinum, whilst silicon had no appreciable effect.

It was found that the presence of a highly charged electric field surrounding the carbon made no difference to the rate of formation of methane at temperatures between 1200° and 1600°, so that no complication is produced in the reaction by ionisation from heated carbon. It is conceivable, however, that a disturbance might have

been caused by carbon vapour distilling from the rod and reacting in the cooler parts of the vessel, or minute particles of carbon are possibly dispersed from the rod and act similarly.

The formation of ethylene which has not before been observed, nor suspected at these low temperatures, has, in this work, been detected at 1200°, and at 1400° it is comparable with the methane formed. The equilibria between the different hydrocarbons and hydrogen are now being investigated by the use of high gaseous pressures.

Part of the incidental expenses of this research have been borne by a grant from the Research Fund of the Chemical Society.

ELECTRO-CHEMICAL LABORATORY,
THE UNIVERSITY, MANCHESTER.

CCV.—*Decomposition of Dry Ozone.*

By DAVID LEONARD CHAPMAN and HERBERT EDWIN JONES.

SPECULATION on the cause of the influence of moisture on chemical change may be said to have been started by H. B. Dixon's announcement of the striking fact that an otherwise explosive mixture of carbon monoxide and oxygen will not inflame after it has been thoroughly desiccated by long exposure to phosphoric oxide. The interest taken in this problem has, in the meantime, been maintained through the discovery (chiefly by Dixon and his pupils) of numerous other examples of water promoting chemical change. H. B. Baker, in particular, has submitted the question to a most exhaustive examination, and the information gathered by him has served to demonstrate the supremely important part played by moisture in chemical changes of the most varied types. Yet owing, no doubt, to the difficulty of obtaining quantitative information bearing on the subject, the phenomenon still remains, in the opinion of many, a mystery. No general hypothesis has, so far, gained universal acceptance. H. E. Armstrong, who holds firmly to Faraday's view that chemical change is essentially electrolytic in character, advances the explanation that water introduces into the system the possibility of electrolytic and reversed electrolytic processes taking place.* J. J. Thomson postulates in the moist gas the

* By electrolysis the author clearly contemplates a process differing in one essential particular from that which is commonly understood by the term. Electrolysis, in its accepted and perhaps restricted sense, can proceed only so long as a transference of electrons is rendered possible through the agency of a

presence of minute drops of water, in the vicinity of which (owing to the high specific inductive capacity of water) the electrostatic forces that bind the atoms together are diminished. Dixon favours, for the present, less general explanations, based on chemical facts.

In attempting to picture the mechanism of a chemical change on which water exerts an accelerative effect, it must be borne in mind that in some few cases of chemical change this agent appears to play an unimportant rôle.

As examples of such actions, the following may be cited:

(*a*) A dry mixture of cyanogen and oxygen inflames as easily as a mixture of the same composition containing moisture (H. B. Dixon, Trans., 1886, **49**, 384).

(*b*) The dried halogens attack mercury with facility (W. A. Shenstone, Trans., 1897, **71**, 471.)

(*c*) Thoroughly desiccated ozone is much less stable than the moist gas (W. A. Shenstone, *loc. cit.*)

It is manifest that a more exhaustive examination of such exceptional cases might, by shedding a fresh light on a relatively neglected aspect of the problem, indicate the right course to be taken in future attempts to discover a solution. The last of the cases quoted above has already received some attention at our hands, and in this research its investigation has been further pursued.

As stated above, Shenstone, in 1897, showed that dry ozone is so unstable that it cannot be prepared from pure oxygen, desiccated with phosphoric oxide, by the silent discharge in the ordinary way. Moreover, the stability of ozone was found by him to decrease as the amount of moisture in the oxygen from which it was produced was diminished. The conclusion was therefore drawn that moisture inhibits the reverting of ozone to oxygen. Armstrong maintained that the peculiar instability of dry ozone, observed by Shenstone, was not caused by the absence of moisture, but was due to the presence of oxides of nitrogen (formed by the continuous action of the discharge from adventitious nitrogen contained in the oxygen), which, as Andrews had shown, immediately destroy ozone. The probability of the truth of Armstrong's contention is supported by the following considerations.

If, as Shenstone asserts, water vapour inhibits the reverting of

conductor of the first class; whereas electrolysis in the sense in which it is employed by Armstrong denotes a process in which the transference of electrons takes place in a molecular grouping across ultramicroscopic distances without the intervention of a metallic canductor. The process conceived by Armstrong is manifestly more sensitive to changes of temperature than ordinary electrolysis.

ozone to oxygen, the fact is a unique example of a new type of catalysis—real negative catalysis. There is no established case of a substance *per se* hindering the progress of a spontaneous chemical change. The so-called negative catalysts operate by modifying an agency which promotes the change.*

Ozone, dried with concentrated sulphuric acid, does not become more stable on its being saturated with water vapour (see Chapman and Jones, Trans., 1910, **97**, 2463, and other publications referred to in the paper).

A point in Armstrong's explanation of Shenstone's result needs further investigation. The explanation assumes that oxides of nitrogen are generated by the discharge with greater facility when the gas is dry. A few simple experiments will serve to demonstrate that this assumption is true, and to indicate the reason for the fact assumed.

Experiment I.†—Oxygen dried with sulphuric acid was passed through a Brodie ozone generator in action, and then through a long, horizontal tube, bent downwards about six inches from its end to permit of the exit being immersed in water. For about eight minutes the ozonised oxygen which had bubbled through the water was quite clear, but after that time it began to be filled with a fine mist, which gradually increased in density. On warming the horizontal glass tube, a dense cloud was formed above the surface of the water. The ozone manifestly contained some hygroscopic substance, which condensed in a film on the surface of the glass and was volatilised on being warmed.

Experiment II.—A wash-bottle, containing concentrated sulphuric acid, was inserted between the ozone generator and the horizontal glass tube. This effectually prevented the formation of a cloud in the ozonised oxygen above the water.

Experiment III.—Dry air, mixed with a little nitrogen peroxide, was passed through water. No cloud was formed. The hygroscopic substance in question is not nitrogen peroxide.

Experiment IV.—Dry air, containing a little nitrogen peroxide, was allowed to mix with ozonised oxygen, and then passed through water. An extremely dense cloud was instantly formed. The

* Inhibitors are apparently divisible into three classes:

(*a*) Photochemical inhibitors the action of which seems to be due to their property of modifying the energy which is the cause of chemical change (Burgess and Chapman, Trans., 1906, **89**, 1399; Chapman and MacMahon, Trans., 1909, **95**, 135, 959, 1717; 1910, **97**, 845; Chapman and Gee, this vol., p. 1726).

(*b*) Inhibitors the action of which depends on their combining with a positive catalyst.

(*c*) Inhibitors which "poison" a solid catalyst (Bredig and others).

† In performing these experiments one of us was assisted by Mr. Edwin Hopkinson.

hygroscopic substance is probably a compound produced by the action of ozone on the nitrogen peroxide, and is most likely nitric acid.

Experiment V.—The cloud produced when ozonised oxygen was passed through water was collected in moist glass wool. The water in the glass wool was found to contain nitric acid, but no nitrous acid.

It is obvious from the above experiments that in the presence of moisture the nitrogen peroxide is removed from ozonised oxygen as nitric acid, which condenses on the surface of the glass, and that the oxides of nitrogen are completely eliminated by the gas being brought into contact with concentrated sulphuric acid, so that the respective causes of ozone, prepared from moist oxygen, being more stable than that formed from the dry gas under similar conditions, and of ozone generated, according to the recommendation of Brodie, in the presence of concentrated sulphuric acid, being in a condition of maximum stability are no longer matters of doubt.

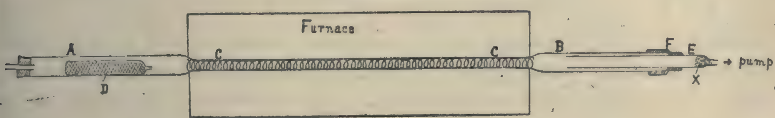
The ozonised oxygen employed by us in all our experiments has been collected in vessels containing concentrated sulphuric acid, and has been left in contact with the acid for several hours before use. We have already shown that the stability of ozone in a mixture of ozone and oxygen, treated in the above manner, is not increased nor appreciably decreased when the mixture is saturated with water vapour. Shenstone's statement that moist ozone is more stable than the partly desiccated gas is therefore incorrect; but it cannot, as yet, be affirmed that the presence of a very small quantity of water vapour is not essential to the progress of the change. The latter statement could, it is true, be made if it were known to be generally the case that the concentration of the water vapour and the rate of change were proportional in those changes for which water vapour is supposed to be necessary. From analogy, we should expect such a relation to hold. It is, however, possible, and has been occasionally assumed to be true (on grounds that are quite insufficient, however) that the rate of change rises very rapidly from zero to a limiting value as the concentration of the water vapour is increased, or, in other words, that the maximum effect can be obtained by the addition of a small amount of vapour. If such were the case, it might be found that, although two samples of ozone, of which one had been dried with concentrated sulphuric acid, and the other saturated with moisture, reverted to oxygen at the same rate, a specimen of the gas, dried by long exposure to phosphoric oxide, would prove to possess enhanced stability. Experiments conducted with the object of testing this possibility will be described later.

The Preparation of Pure Phosphoric Oxide.

The purification of phosphoric oxide by the distillation of the crude oxide in oxygen is both tedious and expensive. The yield is small, and the Jena-glass, after having been once used for the purpose, is completely destroyed. We find that the pure oxide can be prepared with little trouble and much less expense by the burning of phosphorus in air if certain precautions are taken to ensure complete oxidation. The apparatus we use for this purpose is depicted below (Fig. 1).

Two wide pieces of Jena-glass combustion tubing are fused, as shown in the figure, to a long, narrow piece of tube *C* of the same kind of glass. Into the tube *C* a spiral of platinum wire is inserted. The section of the combustion tube, marked *A*, encloses a hard glass tube *D*, which is closed at one end, and drawn out at the other to a narrow opening. This tube is filled with amorphous

FIG. 1.



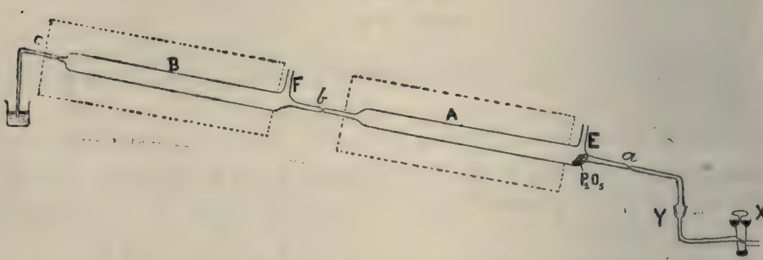
phosphorus. A tube *E* of soft German glass is inserted into *B*, and held in position by a tightly fitting rubber band *F*. *E* contains a plug of glass wool *X*, in order to prevent the finely powdered oxide which collects in *E* from passing further along the tube. The tube *C* is heated to bright redness by means of the furnace, a rapid current of dry air being drawn through it with the aid of a pump connected to *E*. The temperature of the phosphorus in the vessel *D* is then very gradually raised until the vapour escapes and burns at the narrow aperture. By regulating the temperature, the size of the flame of burning phosphorus is kept quite small. If the combustion of the phosphorus is not too rapid, and the supply of air or oxygen is not deficient, the lower oxides of phosphorus are completely oxidised as they pass through the heated tube *C*, and the solid oxide which collects in the tube *E* answers to all the tests for purity given in Shenstone's paper. As Jena combustion glass is not attacked by the vapour of phosphoric oxide, the tube can be used many times for the same purpose. It is possible that the platinum spiral might be dispensed with.

Comparison of the Rate of Decomposition of thoroughly desiccated Ozone with that of Ozone dried with Concentrated Sulphuric Acid.

The oxygen and ozonised oxygen were prepared and collected as described in our previous communication.

The tubes in which the ozonised oxygen was heated were constructed out of Jena combustion glass. Before being filled, they were thoroughly cleansed and dried, all the usual precautions being taken. Two tubes, *A* and *B*, as set up for the purpose of filling, are represented in Fig. 2. Each tube is provided with a side-tube *E* and *F*. Through one of these, say *E*, a plug of phosphoric oxide is introduced, and both the side-tubes are then closed in a similar manner by fusion with the oxy-hydrogen flame. Oxygen is then admitted to the apparatus through the tap *X*. The oxygen passes by way of the ground-glass connexion *Y* through the capillary tube

FIG. 2.



a into *A*, and thence through the capillary tube *b* into *B*; it escapes through the capillary tube *c*, the end of which dips under concentrated sulphuric acid. After all the air has been displaced by oxygen, the ozonised oxygen is permitted to enter, sufficient being passed through to ensure of the gas in *A* being of the same composition as that in *B*. The tubes *a*, *b*, and *c* are then closed before the oxy-hydrogen blowpipe at the constrictions shown in the figure. Both receptacles were then kept in the dark for periods of time varying in the separate experiments from ten days to six weeks.* To decompose the ozone, the tubes are held in a vertical position with the side-tubes *E* and *F* below, and the top portions, indicated in the figure by dotted lines, surrounded with metal jackets (similar to those described in our previous papers), through both of which steam is passed for the same length of time. The time of heating varied from thirty minutes to one hour, these limits being selected because previous experience had shown that the proportion of ozone

* Pure ozone decomposes extremely slowly at the ordinary temperature.

destroyed would, under the conditions of experiment, then lie between one-half and three-quarters of that originally present.

To analyse the contents of a tube, the gas was slowly driven out of the tube through a neutral solution of potassium iodide by a current of carbon dioxide, and after the solution of potassium iodide had been mixed with a little dilute sulphuric acid, the liberated iodine was titrated with a standard solution of sodium thiosulphate. The volume of each tube was measured after the experiment.

Experiment I.—The first pair of tubes, after they had been left in the dark for a fortnight, were completely immersed in a bath of boiling water for half an hour. On analysis of the contents, the tube in which the anhydride was enclosed was found to contain only half as much ozone as that in the other. That this result was due solely to the catalytic influence of the phosphoric oxide on the decomposition of the ozone is amply demonstrated by subsequent experiments.

Experiment II.—This experiment was performed in order to discover if the difference in the rates of decomposition in the two tubes due to the catalytic influence of the drying agent is sufficient to cause the percentage composition of the mixture in the one tube to be appreciably different from that in the other after the tubes had been left in the dark for three weeks. The contents of two tubes which had been left in the dark for the stated time were analysed, and the following results were obtained:

Tube A (containing drying agent).

Ozone corresponding with iodine liberated	=	0·00564 gram.
Volume of the tube.....	=	63 c.c.
Ozone per litre....................................	=	0·0895 gram.

Tube B.

Ozone corresponding with iodine liberated...	=	0·00450 gram
Volume of tube	=	55 c.c.
Ozone per litre	=	0·0818 gram

The proportions of ozone in the two tubes are sufficiently close to show that the catalytic influence of the drying agent on the rate of decomposition of ozone at the ordinary temperature can be ignored. Experiment I, however, demonstrates the necessity of leaving the phosphoric oxide unheated. In the subsequent experiment therefore only the portions of the tubes above the side-tubes were heated in the steam-jackets. As the tubes were almost exactly similar, the proportion of hot to cool gas was approximately the same in both. The results are tabulated on p. 1818.

Number of experiment.	Time of drying	Time of heating. (minutes).	Ozone found. (gram).	Volume. (c.c.).	Ozone per litre. (gram).
I. dry	3 weeks	30	0·0031	64	0·0484
not dry	—	—	0·0027	58	0·0466
II. dry	3 weeks	30	0·00268	55	0·0487
not dry	—	—	0·00274	56	0·0490
III. dry	10 days	45	0·00479	65	0·0737
not dry	—	—	0·00407	54	0·0754
IV. dry	2 weeks	60	0·00377	64	0·0588
not dry	—	—	0·00379	59	0·0642
V. dry	2 weeks	60	0·00443	57	0·0777
not dry	—	—	0·00435	55	0·0791

We deduce from former experiments that the amount of ozone destroyed during the heating would vary in the separate experiments from a little less than one-half to three-quarters of that initially present.

In our opinion, this investigation shows, with a degree of probability that almost amounts to certainty, that small quantities of water vapour do not exert an influence on the thermal decomposition of ozone. For if ozone ceases to decompose when it is absolutely deprived of moisture, it is almost incredible that there should not be a greater difference than is possible from the results of this and the previous research in the ratio of decomposition of the gas dried with phosphoric oxide, on the one hand, and saturated with water vapour, on the other.

The fact established in our last paper that, by increasing the partial pressure of the oxygen mixed with the ozone, no alteration in the rate of decomposition of the latter results, shows that the oxygen used in the experiments contained no catalyst for the change. That a catalyst was adhering to the inner surface of the glass and was volatilised when the tubes were heated to 100° is also improbable, firstly, because the tubes were strongly heated in a current of dry air before being filled, and secondly, because the presence of such a catalyst would have been indicated by discordant results. The experimental evidence favours the view that the decomposition of ozone can proceed by itself, without the intervention of any other substance.

The view expressed by Dixon years ago, and later supported by Shenstone, that some chemical changes can proceed without the aid of water, receives from this research substantial support. Furthermore, the work being quantitative in character, it enables us to take a step forward by expanding Dixon's conclusion with the statement that in one chemical change, at least, not only is the presence of water unnecessary, but it attended by an inappreciable effect.

To prevent misunderstanding, it may be well to point out that this research is no ground for the conclusion that water is not a weak catalyst for the decomposition of ozone. There are, on the contrary, strong reasons for thinking that it may be. Ozone, when it is passed into concentrated aqueous potassium or sodium hydroxides at a low temperature, furnishes yellowish-brown solutions, which are very unstable, rapidly evolving oxygen when the temperature is raised. The acidified yellow solutions do not contain hydrogen peroxide. In all probability therefore the solutions contain salts of a weak acid of the composition expressed by the formula H_2O,nO_3. It is by no means improbable that it is the ionised portion of the salt which is unstable, and that the changes in the solution can accordingly be represented by the equations:

$$2OH' + 2O_3 \rightleftharpoons 2HO_4' \longrightarrow H_2O + 3O_2,$$

it being assumed, for the sake of argument, that the ions contain but one molecule of ozone. If the above view of the decomposition of ozone by alkalis is correct, water and even steam must in some measure accelerate the reverting of ozone to oxygen. In the presence of moisture, most of the ozone is destroyed, however, without the assistance of the water, the number of hydroxyl ions being so small that their catalytic effect cannot be detected. It being assumed that the law of mass holds, the rate of decomposition of ozone would then be given by the equation:

$$\frac{d[O_3]}{dt} = A[O_3]^2 + B[O_3]^2[OH],$$

in which A and B are constants. In the above equation, the last term must be supposed to be negligible owing to the finite value of B and the infinitely small value of [OH].

THE SIR LEOLINE JENKINS LABORATORIES,
JESUS COLLEGE, OXFORD.

CCVI.—*The Acid Character of Gallotannic Acid.*

By RAMNI PANIKER and EDMUND STIASNY.

IN spite of the large amount of experimental data which has accumulated on the subject of late, the chemical constitution of gallotannic acid is not settled beyond controversy. The problem naturally resolves itself into the following questions:

1. Is gallotannic acid a single substance or a mixture?
2. Is it a real acid, that is, one containing a free carboxyl group?

3. How is the optical activity to be accounted for?

As to its homogeneity, different authors assume that it is a mixture of closely allied substances. Walden (*Ber.*, 1897, **30**, 3151) drew the above conclusion by studying its dialytic behaviour and the properties of the different products obtained by fractional precipitation. He also observed different optical activities for the various samples purified by different methods (compare Rosenheim and Schidrowitz, Trans., 1898, **73**, 885; Dekker, *Ber.*, 1906, **39**, 2497; and Nierenstein, *Chem. Zeit.*, 1909, **33**, 126). Aweng (*Rev. Int. Falsif.*, 1898, **11**, 29) arrived at the same conclusion by studying its condensation products with formaldehyde. By means of capillary analytical experiments, Kunz-Krause (*Schweiz. Wochensch. Chem. Pharm.*, 1898, No. 38) found that a 5 per cent. aqueous solution of pure gallotannic acid gave two distinct capillary zones, leading him to the same conclusion as the previous authors. Finally, Nierenstein (*Ber.*, 1905, **38**, 3641; 1907, **40**, 917; 1908, **41**, 77, 3015; 1909, **42**, 1122, 3552; 1910, **43**, 628; *Chem. Zeit.*, 1907, **31**, 72; 1909, **33**, 15) explains the properties of gallotannic acid as due to a mixture of digallic acid and leucotannin.

As regards the acid character of gallotannic acid, expressed by the presence of a free carboxyl group in the well-known Schiff's formula, $C_6H_2(OH)_3{\cdot}CO{\cdot}O{\cdot}C_6H_2(OH)_2{\cdot}CO_2H$, several authors hold different views on the subject. Thus Böttinger (*Ber.*, 1884, **17**, 1503) found that benzoylgallotannic acid is insoluble in alkali. Dekker (*loc. cit.*) showed that the acetyl compound was insoluble in excess of *N*-sodium hydroxide even on boiling. Dekker therefore argued that no free carboxyl group could be present in the molecule, and cites the work of Walden (*Ber.*, 1898, **31**, 3170), who, from his electrical conductivity experiments, found such low figures for the affinity constant that he assumed gallotannic acid to be of a non-electrolytic nature, the small experimental figures being ascribed to impurities.

The present paper deals mainly with the acid character of gallotannic acid, but the question of its homogeneity is also considered.

Experimental.

The determination of the hydrion concentration of gallotannic acid was carried out by Fraenkel's method (*Zeitsch. physikal. Chem.*, 1907, **60**, 202), which is based on the evolution of nitrogen from diazoacetic ester, due to the catalytic influence of hydrions:

$$N_2{:}CH{\cdot}CO_2Et + H_2O = OH{\cdot}CH_2{\cdot}CO_2Et + N_2.$$

In investigations of a like nature (Spitalsky, *Zeitsch. anorg. Chem.*, 1907, **54**, 265; Holmberg, *Zeitsch. physikal. Chem.*, 1908,

62, 726), this method has given very satisfactory and concordant results.*

The velocity of the reaction is calculated from the volume of nitrogen evolved at definite intervals of time:

where $$k = \frac{1}{0{\cdot}4343t}.\log\frac{a}{a-x},$$

a = total value of nitrogen corresponding with a given concentration of the ester;

x = volume of nitrogen evolved in time t.

The use of a glass flask was precluded by the appreciable neutralisation of hydrogen ions due to the alkalinity of the glass, especially in the case of weak organic acids. Quartz was found to be a satisfactory substitute for glass, and all recorded experiments were performed in a quartz flask.

Purification of Gallotannic Acid.

Method I.—Fifty grams of Kahlbaum's "extra pure tannic acid" were dissolved in 500 c.c. of water, and precipitated by means of a saturated solution of pure sodium chloride. The precipitate was repeatedly washed on the filter with the salt solution, again dissolved in a small quantity of water, and salted out. This salting-out process was repeated half-a-dozen times, and the product finally dried in a vacuum at a low temperature. The dried mass was then extracted with freshly distilled methyl acetate, the filtrate evaporated in a vacuum at the laboratory temperature, and dried until free from all traces of the solvent. The sample so obtained was by no means free from traces of gallic acid, which are invariably carried down with the precipitate during the salting-out operations.

Method II.—This method was that described by Rosenheim and Schidrowitz (Trans., 1898, **73**, 882), but depending as it does on the phenomenon of distribution of a substance between two solvents, it is by no means a perfect one.

The small amount of gallic acid which is always left behind in the purified sample introduces a greater variation in the degree of acidity than in the values obtained by the authors above referred to for the specific rotatory power of the substance.

Method III.—(1) This consisted in neutralisation by means of sodium hydrogen carbonate and extraction with ethyl acetate.†

The commercial product was first purified from all resinous and

* For the preparation of the diazo-ester and a detailed description of the apparatus used, see Klages, *Ber.*, 1903, **36**, 1506; Fraenkel, *Zeitsch. physikal. Chem.*, 1902, **40**, 202; 1904, **47**, 185.

† This method was suggested to us by Mr. A. G. Perkin, to whom we are indebted for the great interest he took in this work.

colouring matter by repeatedly shaking the acetone solution with ether (as in method II), and the residue dried as before. The product so obtained was dissolved in a small quantity of water. To avoid the presence of any normal carbonate, a current of carbon dioxide was passed through a saturated solution of sodium hydrogen carbonate for about twenty minutes. The aqueous solution of the tannin was similarly freed from oxygen, and neutralised with the bicarbonate solution until it was faintly alkaline to litmus.

The solution was then extracted three times with freshly distilled ethyl acetate. The extract so obtained was washed with small quantities of water until free from traces of alkali, concentrated in a vacuum at the ordinary temperature, and precipitated by means of pure dry benzene. The white precipitate so obtained was boiled with benzene to remove traces of the ester, filtered, and finally dried in the vacuum oven for four hours. The acidity of the product was then tested.

(2) The above purification was then repeated, using more of the bicarbonate solution, so that the liquid was more strongly alkaline than in the previous case. The product so obtained was tested for acidity.

(3) Repeating the process of purification for a third time, the aqueous solution of the substance was finally precipitated with the bicarbonate solution, and extracted as before. The product was again examined as in the two previous cases.

(4) The filtrate obtained after precipitation with the bicarbonate solution was partly neutralised with hydrochloric acid, and extracted with ethyl acetate, washed, concentrated, and finally precipitated with benzene. In the place of a white, amorphous precipitate, as obtained in the last case, a dark, viscous mass was produced, which, when dried, was greyish-white. The acidity of this product was also noted.

Owing to the insolubility of sodium gallate and other allied salts in ethyl acetate, this method is an excellent means of purifying gallotannic acid. The products so obtained are invariably free from even traces of sodium.

Catalysis of Ethyl Diazoacetate.

Weak electrolytes, tested according to this method, yielded the following values for k:

TABLE I.

	k.
Gallic acid	0·01337
Protocatechuic acid	0·01122
β-Resorcylic acid	0·04999
Salicylic acid	0·0751
Pyrogallol	0·000081
Boric acid	0·000065

A summary of the results obtained with gallotannic acid is given in table III.

The following table gives details of a typical experiment with gallotannic acid:

TABLE II.

Catalyst: Gallotannic acid (0·3244 gram); method II; fourth purification.

Concentration of ester, 0·2050 gram in 20·2 c.c. Mean pressure, 749·6 mm. $a=40·28$ c.c. ($x'=x$ at N.T.P.)

(mins.).	Temp.	x c.c.	x' c.c.*	$a-x'$.	k.
30	14·0°	2·605	2·41	37·87	0·002052
40	13·5	3·60	3·33	36·95	0·002158
50	13·5	4·60	4·26	36·02	0·002236
60	13·5	5·50	5·09	35·19	0·002252
70	13·5	6·40	5·91	34·37	0·002267
80	13·5	7·30	6·74	33·54	0·002289
90	13·5	8·20	7·57	32·71	0·002313
100	13·5	9·10	8·40	31·88	0·002339
110	13·5	9·90	9·14	31·14	0·002340
120	13·5	10·605	9·79	30·49	0·002321
130	13·5	11·40	10·52	29·76	0·002328
140	13·5	12·20	11·26	29·02	0·002342
150	13·5	12·85	11·86	28·42	0·002325
160	13·5	13·60	12·56	27·72	0·002336
170	13·5	14·30	13·20	27·08	0·002336
180	13·5	15·00	13·84	26·44	0·002339
225	13·5	18·00	16·62	23·66	0·002365
250	13·5	19·50	18·00	22·28	0·002369
265	13·5	20·40	18·83	21·45	0·002377
280	13·0	21·20	19·66	20·62	0·002391
300	13·0	22·30	20·68	19·60	0·002396
330	13·0	23·65	21·93	18·35	0·002383
360	13·0	25·05	23·23	17 05	0·002388

Mean value of $k=231\times10^{-5}$. $C_H=6\times10^{-5}$.†

* In calculating this quantity allowance must, of course, be made for the tension of aqueous vapour as x is measured moist.

† The value of C_H is calculated by using Fraenkel's factor for aqueous solutions: $k/C_H=38·5$.

TABLE III.

The values of k are compared with the specific rotatory power of each sample.

Purification. Method.	Order.	Conc., gram in 20·2 c.c.	k.	C_H.	$[\alpha]_D^{17}$.	Remarks.
,, I.		0·322	328×10^{-5}	$8{\cdot}5 \times 10^{-5}$	—	Rich in gallic acid
,, II.	1st	0·322	422×10^{-5}	$11{\cdot}5 \times 10^{-5}$	+73·29°	Rich in gallic acid
,, ,,	2nd	0·33832	240×10^{-5}	$6{\cdot}2 \times 10^{-5}$	+72·12	Contained traces of gallic acid
,, ,,	3rd	0·32888	198×10^{-5}	$5{\cdot}1 \times 10^{-5}$	+72·37	Seems free from gallic acid
,, ,,	4th	0·3244	231×10^{-5}	$6{\cdot}0 \times 10^{-5}$	+70·90	Seems free from gallic acid
,, III.	1st	0·33472	224×10^{-5}	$5{\cdot}8 \times 10^{-5}$	+56·76	Free from even traces of gallic acid
,, ,,	2nd	0·30128	148×10^{-5}	$3{\cdot}8 \times 10^{-5}$	+64·72	Free from even traces of gallic acid
,, ,,	3rd	0·31592	112×10^{-5}	$2{\cdot}9 \times 10^{-5}$	+69·60	Free from even traces of gallic acid
,, ,, ex-tracted from filtrate [III(4)]		0·32408	214×10^{-5}	$5{\cdot}6 \times 10^{-5}$	+65·10	Free from even traces of gallic acid

A Comparative Review of the Different Methods of Purification of Gallotannic Acid.

Method I (Precipitation by means of sodium chloride) is not sufficient to get rid of all gallic acid from the commercial sample. A sample which was salted out twenty-four times still gave, after extraction with ethyl acetate or alcohol, a faint gallic acid reaction with potassium cyanide. This fact is clearly shown by the high values obtained for k and C_H.

Method II (Unequal distribution of gallic and gallotannic acids in ether and acetone) is a tedious one, and it is never possible to obtain a sample completely free from gallic acid. It can be seen from the tables that as the purification proceeds, the velocity constant, and consequently the hydrion concentration, both diminish and approximate to a constant value.

Method III (Insolubility of sodium gallate in acetic ether) is by far the best which has been employed for the complete separation of gallic acid impurity from gallotannin. Unlike method II, even

the first fraction is so thoroughly free from gallic acid that we might with sufficient justification state that the hydrogen concentration $5 \cdot 8 \times 10^{-5}$ (see table) is outside the influence of gallic acid.

Conditions which Govern the Progress of the Reaction.

The temperature-coefficient of the reaction, judging from analogy to similar catalytic reactions, is by no means negligible. A difference of 0·25 to 0·5 which the thermostat had shown during the course of some experiments is perhaps sufficient in the majority of cases to account for the deviation which in certain cases K exhibits from its mean value.

The rate of evolution of nitrogen as measured by the nitrometer readings is considerably influenced by the character of the solution as well. When it is of a colloidal character, as with gallotannic acid solutions, a considerable amount of the gas is retained on the surface of the solution in the reaction flask, which consequently escapes measurement, and leads to a variation in the observed rate of the reaction.

Affinity Constant and Optical Activity.

No proportionality seems to exist between the specific rotatory power of the substance and its velocity constant. This relationship seems to depend largely on the method of purification employed, and is also governed by the amount of gallic acid impurity left in the sample.

Purification by method II, based on the work of Rosenheim and Schidrowitz, gives a substance with constant values for k and $[\alpha]_D$, and judged alone it would seem to indicate that gallotannic acid is an acid of constant rotatory power and of definite acidity. When we proceed to purify the same substance according to method III, a perceptible increase in the value of $[\alpha]_D$ manifests itself as the value of k diminishes with the order of purification. This would naturally indicate a partial differentiation of the proximate constituents.

This method has already been stated to yield a product free from gallic acid. As is shown by the figures given in the table, the value of $[\alpha]_D$ in this case is not so high as that of any of the purified samples under method II. Further, the acidity of the products in this case approximate to a minimum value. Moreover, by extracting the neutralised product from the mother liquor according to method III(4), a substance is produced which gives a velocity constant with almost double the value obtained in the case of the third sample (method III).

If these are two different chemical individuals, then naturally the one must be twice as strong as the other in its chemical affinity. These facts do not allow of the conclusion that we are here dealing with a homogeneous substance.

To compare the degree of dissociation of gallotannic acid with that of any other weak organic acid like gallic, we should naturally have some idea of the molecular weight of the substance in aqueous solution. According to Sabanéeff, gallotannic acid has a molecular weight of 1322 in water, but it is evident that this number has no molecular significance, inasmuch as the ordinary osmotic methods cannot be used for the determination of molecular weight of substances in a colloidal solution.

The fact that gallotannic acid can be divided into two parts by saturating the solution with sodium hydrogen carbonate, the one part being soluble in ethyl acetate, whilst the other forms a sodium salt which, on acidification, is capable of being extracted with ethyl acetate, points to the fact that we have here to deal with a mixture of two or more substances of different degrees of acidity.

This view is favoured by the fact that the substance extracted direct after neutralisation with sodium hydrogen carbonate is only half as acid as that which is set free on acidifying the sodium salt in solution. The difference in the values of k and $[\alpha]_D$ shown by different samples purified after different methods also supports this view.

Another observation may also be mentioned, although it still wants further investigation. If the white, amorphous precipitate obtained by salting out the solution of gallotannic acid is dissolved in absolute alcohol and treated with an absolute alcoholic solution of potassium acetate, a precipitate is formed, which in similar cases has been shown by A. G. Perkin (Trans., 1908, **93**, 129) to be the potassium salt of the acid or an oxonium salt. This precipitate was washed with absolute alcohol and treated with pure ethyl acetate to remove traces of any free gallotannic acid. It was then filtered, dried, and analysed. The following analytical figures were obtained, which, when calculated, seems to agree with the unimolecular formula $C_{14}H_9O_9K$ for the potassium salt:

0·4383 gave 0·1032 K_2SO_4. K = 10·6.

$C_{14}H_9O_9K$ requires K = 10·8 per cent.

The optical inactivity of this potassium salt and the optical behaviour of gallotannic acid, prepared from the former, will form the subject of a special paper, which, we hope, will throw some light on the constitution of gallotannic acid.

Summary.

The foregoing experiments seem to be in favour of the view that gallotannic acid is a mixture of two or more chemical individuals, possibly of an allied character (compare Kunz-Krause, Walden, Aweng, Nierenstein). On the other hand, our observations do not agree with the view of Böttinger, Walden, and Dekker that gallotannic acid has no free carboxyl group, as the affinity constant found by us is distinctly of a higher order than those of phenols.

UNIVERSITY, LEEDS.

CCVII.—*Bimolecular Glycollaldehyde.*

By NIAL PATRICK McCLELAND.

IT has often been the custom to make a distinction between "association" and "polymerisation." The former has been regarded as a physical phenomenon consisting in the aggregation of whole molecules, whereas the latter is generally classed as a chemical process, and the constitution of the polymerised forms is expressed in terms of atomic linking.

At present the prevailing view appears to be that the two phenomena are of the same kind, differing only in degree, and it has been found necessary to evolve hypotheses of "latent," "auxiliary," and "contra" valencies to explain the constitutions of the resulting substances. Practically the question may be merely one of stability, that is to say, the difference between "association" and "polymerisation" as ordinarily defined may lie only in the fact that polymerised forms can be definitely isolated as such between wide limits of temperature, pressure, and so on, whereas the degree of association depends entirely on the conditions.

Now Fenton and Jackson observed (Trans., 1899, **75**, 575) that the molecular weight of crystalline glycollaldehyde in a freshly prepared aqueous solution is 120, that is to say, double the value expected from the formula $HO{\cdot}CH_2{\cdot}CHO$, and, further, that it gradually falls to the normal value on keeping.

Similar behaviour has been observed in the related substances glyceraldehyde and dihydroxyacetone by Wohl (*Ber.*, 1898, **31**, 2394) and Bertrand (*Compt. rend.*, 1899, **129**, 341) respectively.

At Dr. Fenton's suggestion the author has investigated this change of state in the case of glycollaldehyde with the object of ascertaining its general character as an association or polymerisation phenomenon in the sense indicated above.

Bertrand concluded that the change observed by him was due to molecular dissociation. He seems to have based his conclusion partly on an observation that the molecular weight of the liquid formed by the melting of crystalline dihydroxyacetone was almost normal in solution, suggesting that the liquid was the unassociated form, and partly on the fact that, although the crystalline substance is sparingly soluble in alcohol and ether, yet on warming it readily dissolves, and does not recrystallise on cooling; reasons are given below for concluding that the former observation is erroneous; the latter can obviously be easily explained otherwise.

Wohl suggested that the crystalline form is a sort of acetal formed from two molecules, thus:

$$\begin{array}{l} CH_2\cdot OH \\ CHO \end{array} + \begin{array}{l} CHO \\ CH_2\cdot OH \end{array} = \begin{array}{l} CH_2\text{—}O\text{—}CH\cdot OH \\ CH(OH)\cdot O\cdot CH_2 \end{array}$$

$$\text{or possibly} = \begin{array}{l} CH(OH)\cdot CH\cdot OH \\ CH(OH)\cdot CH\cdot OH \end{array}$$

in which case the change in aqueous solution would be due to hydrolysis, with the formation of an ortho-aldehyde.

The investigation was carried out in the following way:

First, the dissociation of glycollaldehyde in aqueous solution was investigated with a view to ascertaining the influence of dilution on the rate.

Next, the molecular state in other solvents was studied. The solvents tried were methyl and ethyl alcohols, acetone, acetonitrile, pyridine, formic and acetic acids.

It was expected that if the change was due to hydrolysis, alcohols would bring it about almost as readily as water, possibly with the formation of acetals of the normal type, the other solvents not at all; whilst on the supposition that the bimolecular state is an example of association, solvents would probably be effective in the order of their dissociating powers.

The vapour density was also determined somewhat above the boiling point, and Mr. Purvis kindly photographed the absorption spectra of the two forms in solution.

The glycollaldehyde was prepared by the method described by Fenton (Trans., 1905, **87**, 817). A pyridine solution is formed from dihydroxymaleic acid, and is distilled in a vacuum; finally, glycollaldehyde crystallises out on nucleating the syrup obtained by evaporating the pyridine in a desiccator. During the latter part of the distillation (when all the pyridine has passed over), crystals are frequently formed in the tube, showing that they can form spontaneously.

Crystals have also been obtained from an aqueous solution, but any trace of impurity seems to prevent their formation.

The glycollaldehyde so obtained melts at 96—97°, forming a syrupy liquid, which, when cooled, does not crystallise for several days. This liquid appears to be identical with the syrup mentioned above. The yield is very poor, about 0·5 to 1 per cent. of the calculated (starting from tartaric acid). Owing to the cost, it was essential to work on a very small scale throughout.

Dissociation Rate in Water.

This was studied by making successive determinations of the apparent molecular weight in aqueous solution, using the cryoscopic method. Between readings, the solution was kept surrounded by ice.

The continual change of temperature necessary for each reading caused the experimental error to be somewhat great.

t = time of observation in minutes after the first reading.

m = calculated molecular weight.

C = concentration of double molecules, taking the initial value as the unit,

so that $C = \dfrac{M - 60}{60}$,

$k = \dfrac{1}{t' - t} \log_e \dfrac{C}{C'}$, where C' and t' refer to the last reading given.

In this way it was hoped that the error due to the fact that it took an appreciable time to dissolve the whole of the substance would be minimised.

The molecular depression for water was taken to be 18·7.

(1) 0·4212 gram of substance in 20·80 of water (1 in 49·4).

t.	Δ.	*m.*	*C.*	*k.*
—	0·387	114·1	0·902	0·0023
30	0·401	110·1	0·835	0·0020
60	0·417	106·1	0·768	0·0020
95	0·429	103·0	0·717	0·0020
130	0·438	101·0	0·683	0·0021
160	0·449	98·5	0·642	0·0021
220	0·471	93·9	0·565	0·0022
270	0·489	90·4	0·507	—

Mean, $k = 0·00210$.

(2) 0·1831 gram in 16·56 (1 in 90·4).

t.	Δ.	*m.*	*C.*	*k.*
—	0·182	113·6	0·873	0·0030
60	0·198	104·4	0·740	0·0030
130	0·219	94·4	0·573	0·0028
190	0·231	87·4	0·457	0·0023
315	0·256	80·8	0·347	0·0033
330	0·259	79·8	0·330	—

Mean (excluding 4th value), $k = 0·00303$.

(3) 0·1128 gram in 31·91 (1 in 283).

It was found that $k=0{\cdot}00561$.

The above results show that the reaction is, as might be expected, unimolecular, that is, $C_4H_8O_4 \longrightarrow 2C_2H_4O_2$, and that the rate increases with the dilution.

The effect of temperature has not been studied quantitatively, but it has been observed that at 20° the change takes place with extreme rapidity.

So far as can be observed, the dissociation in dilute solutions is complete, but since crystals can be obtained from an aqueous solution it follows that association must take place in strong solutions.

The Liquid Form in Water.

The molecular weight in water was determined.

	Solvent (grams).	Substance (gram).	Δ^t.	M.W.	
1.	25·02	0·1946	0·118	123·0	fresh solution
			0·139	100·8	on keeping
			0·149	97·4	on keeping
2.	15·43	0·1049	0·119	106·9	fresh solution
			0·194	65·5	on keeping

Whence it appears that the liquid form exhibits the same behaviour as the solid form.

Bertrand states, as mentioned above, that the molecular weight of a solution in water of liquid dihydroxyacetone is almost normal (105, normal value = 90). He mentions, however, that it took twenty-five minutes to cool the solution to freezing point. If, as appears possible, he started with the solution at the ordinary temperature, it is natural that dissociation would take place very rapidly at first.

Molecular State in Solvents other than Water.

The solvents are taken in the order of their dissociating powers. All were purified carefully before using.

Formic Acid.

The cryoscopic method was used for this solvent. Const. = 27·7.

Solvent (grams).	Substance (gram).	Δ^t.	M.W.
22·13	0·1517	0·279	67·5
		0·439	42·9

That the molecular weight falls below 60 may be explained by assuming that esterification takes place in addition to dissociation,

one molecule of bimolecular glycollaldehyde giving rise to 4 molecules, 2 of unimolecular formate and 2 of water.

The same results were obtained when acetic acid was used as solvent; it was noticed that the apparent molecular weight gradually sank to 30.

It is concluded that in formic and acetic acids dissociation readily takes place, apparently accompanied by esterification.

Methyl Alcohol.

The molecular weight was observed by the boiling-point method, using Beckmann's apparatus.

The molecular elevation is 8·80.

	Solvent (grams).	Substance (gram).	E.	M.W.	
1.	40·61	0·2163	0·058	81·0	after 30 minutes' boiling
			0·074	63·5	,, 50 ,, ,,
2.	40·02	0·2828	0·059	105·6	,, 15 ,, ,,
			0·079	79·0	,, 30 ,, ,,
			0·091	68·5	,, 45 ,, ,,

It appears, then, that dissociation takes place in methyl alcohol on boiling, although far less rapidly than in water and formic acid.

The experimental error was too great to permit the rate to be determined satisfactorily.

Acetonitrile.

The pure solvent boiled at 80·0°. The molecular elevation is 14·39.

	Solvent (grams).	Substance (gram).	E.	M.W.	
1.	40·92	0·2898	0·090	113·0	after 20 minutes' boiling
			0·134	76·0	,, 45 ,, ,,
2.	20·38	0·3330	0·156	108·2	,, 20 ,, ,,
			0·178	95·0	,, 40 ,, ,,
			0·201	84·0	,, 60 ,, ,,
			0·236	71·6	,, 90 ,, ,,

Therefore, dissociation takes place in acetonitrile somewhat less rapidly than in methyl alcohol.

Ethyl Alcohol.

The molecular weight in a fresh solution was found by using Walker's method:

0·3871 gram in 15·8 c.c. gave E 0·31°. M.W. = 123·1.

0·1560 ,, 19·5 c.c. ,, E 0·11°. M.W. = 113·5.

A solution was then boiled under reflux for five hours. After this time the molecular weight was determined, and it was found that almost complete dissociation had taken place:

0·4004 gram in 32·39 grams gave E 0·180°. M.W. = 79·0.
0·4004 „ 32·39 „ „ E 0·192°. M.W. = 74·1 thirty-five minutes later.

Acetone.

A solution was boiled for five hours, as before.

Substance (grams).	Solvent (gram).	E.	M.W.
32·39	0·4004	0·192	106·0
		0·197	103·6
37·96	0·2660	0·136	85·0

A solution kept at the ordinary temperature for three weeks showed no trace of dissociation.

Pyridine.

The molecular state in pyridine was determined by Blackman's method (Trans., 1904, **85**, 1474) under diminished pressure, using carbamide (M.W. = 60) as comparative substance. The results appeared to indicate that the substance was dissociated.

Vapour Density.

Hofmann's method was employed.

Since glycollaldehyde on heating tends to polymerise into a brown gum, it was necessary to heat rapidly; even so, however, traces of "browning" appeared.

This rapid heating prevented the mercury from being properly heated throughout. These two errors tend to cancel one another, and no allowance has been made for them.

The heating liquid used was aniline, which boils at 182°.

This temperature is well above the boiling point of glycollaldehyde, which observations in a vacuum place in the neighbourhood of 150°:

(1) 0·0218 gram gave 48·6 c.c. of vapour at 182°.

Barometer's height, 782 mm.

Height of mercury column, 602 mm. Correction for expansion, 19 mm.

Vapour pressure of mercury at 182° = 12 mm.

So pressure of the vapour = 187 mm.

Hence vapour density = 33·8.

(2) 0·0141 gram gave 43·7 c.c. of vapour at 182°.

Barometer height, 758 mm.

Height of mercury column, 622 mm. Correction, 20 mm.

So pressure of the vapour = 144 mm.

Hence vapour density = 31·5.

The vapour is therefore unassociated about 30 degrees above the boiling point.

The above results, namely, dissociation in solvents usually classed as dissociating, some of which have no hydrolysing power, coupled with dissociation in the vapour state, and with return to the bimolecular state on condensation, appear to point to the conclusion that in the bimolecular state we are dealing with the phenomenon of association, that is, linking of two whole molecules, rather than chemical interaction between them. The abnormal feature of this case lies in the fact that dissociation is by no means immediate. It is possible, however, that in other cases, where a substance has been found partly associated in a solvent, true equilibrium may not have been reached.

An observation has been made, showing a chemical difference between the two forms.

Action of Phenylhydrazine.

When phenylhydrazine is added to an aqueous solution, a yellow osazone (m. p. 169—170°) separates; if, however, phenylhydrazine is added to a fresh alcoholic solution, no action whatever takes place, and on evaporating the alcohol the aldehyde appears to have dissolved in the phenylhydrazine.

This suggests that the CO group is absent from the associated form.

Absorption Spectrum.

A $N/100$-solution in alcohol of the solid glycollaldehyde was made, and its absorption spectrum observed in the usual way, through varying thicknesses.

Four well-marked bands were observed, and through a thickness of 15 mm. the centres of maximum absorption of the bands were λ 2615, λ 2550, λ 2495, λ 2445, and through a thickness of 42 mm. general absorption began at λ 2645.

A $N/100$-solution in water was also examined; no bands were observed. The positions at which general absorption began through 15 mm. and 45 mm. were λ 2270 and λ 2290 respectively.

These results prove that the conditions of the dissolved substances were entirely different in the two cases (for it is extremely unlikely that the bands are due to the solvent itself).

Specific Gravity and Refractive Power of the Liquid Form.

At 100, 0·2035 c.c. weighed 0·2729 gram. D = 1·372.
0·3158 c.c. „ 0·4300 „ D = 1·361.
Mean............1·366.

At 16° the density was obtained by measuring the length which a known weight of the liquid form occupied in a calibrated tube.

It was found that 0·6122 gram of mercury occupied 5·72 cm. of the tube,

and (1) 0·1540 gram substance occupied 14·12 cm. D = 1·385.
(2) 0·1277 " " " 11·60 cm. D = 1·397.
Mean............1·391.

From the above, by extrapolation, the density at 11° = 1·393.

At 11° it was observed that $\mu_\omega = 1·4811$ (Lorentz formula).

Hence $M_D = 24·51$.

Twice the calculated value for $HO·CH_2·CHO$ is 26·39.

From the above results the author concludes that the abnormal molecular weight of glycollaldehyde in the pure form is due to a phenomenon which is on the border line between "association" and "polymerisation," that is, association where the associated form is not extremely unstable.

It is suggested that the constitution in the bimolecular state is represented by the formula $HO·CH_2·CH{<}^{O}_{O}{>}CH·CH_2·OH$, the calculated value for the refractive power for which is 24·82 (not making any allowance for the ring formation), agreeing fairly well with the observed value. Similar formulæ suggest themselves in the cases of crystalline dihydroxyacetone and glyceraldehyde. Support is given to this hypothesis by the fact that some ketones (where no acetal formation is possible) and amides are associated. Aldehydes also appear to be capable of bimolecular association, for it has been observed that when gaseous formaldehyde is passed into chloroform (an extremely non-dissociating solvent) a substance having the formula $C_2H_4O_2$ is obtained (*Pharm. Zeit.*, 1904, **49**, 608). In these cases the cohesion between the two molecules is far less intense than in the case considered above, in which it perhaps is due to some influence exerted by the hydroxyl group.

If the above constitution is assumed, the behaviour of the substance can be completely accounted for.

In the first place, it appears that solutions which give rise to absorption bands in the ultra-violet are generally those of substances which contain unsaturated rings admitting of alternations of linking, the bands being perhaps due to vibrations from one form of linking to another. In the case of glycollaldehyde, this can occur through the alternation of the forms $C{<}^{O}_{O}{>}C$ and $C\colon O\colon O\colon C$. Secondly, it appears probable that a system of the above type is not very firmly linked up, and therefore will be liable to rupture if intense vibrations are set up.

It is suggested that solvents have the power either to intensify or damp the vibrations of the molecules of solutes, on account of the vibrations of their own molecules. Where the vibrations are intensified the solvent is a dissociating one, and it is particularly noticeable that those solvents are most strongly dissociating the molecules of which are most strongly associated, and so are in a state of vibration of a character similar to those of the solute.

In conclusion, the author desires to record his great indebtedness to Dr. Fenton for his very kind advice throughout the work, and to Mr. Purvis for photographing the absorption spectra and suggesting their interpretation.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CCVIII.—*The Aerial Oxidation (Rusting) of Metals.*

By WYNDHAM ROWLAND DUNSTAN and JOHN RICHARD HILL.

SINCE the last communication (Trans., 1905, **87**, 1548; also Proc., 1907, **23**, 63) was made to the Chemical Society on this subject by one of the present authors in continuation of previous work, from which it was concluded that the presence of carbonic acid or of any acid is not essential to the rusting of iron, for which only dissolved oxygen and iron are the necessary conditions, several other investigators have made contributions in this field, the most important of these being that of Tilden (Trans., 1908, **93**, 1356), who has confirmed this conclusion. For the most part the other contributions have been made with the object of supporting the former view that carbonic acid is an essential feature in this process. The results presented by one of the present authors and his collaborators, by Whitney, and by Tilden, are, however, conclusive in showing that the older view must be abandoned. There is, moreover, no reason to believe that the mechanism of the reaction in the case of the rusting of iron differs essentially from that of other metals. There are a few points in which it has been supposed to differ, but it will now be shown that these are unimportant, and in no sense radical differences. What has now to be sought is a satisfactory explanation of the fact of the aerial oxidation, not only of iron, but of all those metals which possess this property.

In the previous paper it was held as a working hypothesis that the rusting of iron involves the intermediate formation of hydrogen peroxide, as in the case of the other metals. Support for this view

was obtained from the action of the various reagents which inhibit rusting and also destroy hydrogen peroxide, and as a working hypothesis it has done good service.

The electrolytic (dissociation) theory advocated by Whitney, Walker, and others has been discussed in the previous paper, and shown not to be supported by fact. It is based on the assumption that iron passes into solution in pure water by replacement of the hydrogen ions before rusting takes place. Tilden also apparently adopts this theory, but combines with it the view that impurities in the iron play an important rôle by setting up local electrolytic action. According to the electrolytic (dissociation) theory, however, pure iron should dissolve in pure water. The question of impurities, and the electrolytic action produced by these, is quite a distinct problem. The more recent fact established by Lambert and Thomson (Trans., 1910, **97**, 2426) that pure iron does not rust in pure water containing dissolved oxygen, is opposed to the electrolytic (dissociation) theory of rusting, and is in accordance with the general experience that chemical change is invariably greatly retarded when highly purified materials are employed. Tilden also noticed a marked difference in behaviour between iron which has previously been treated with chromic acid and that which has not, an important point which is dealt with in the present paper.

The observation of these authors that slightly impure iron rusts without the presence of carbonic acid, or of any other acid, supports the conclusion arrived at by one of us in previous communications.

All these hypotheses and theories claim with varying degrees of success to explain the action of the various reagents which inhibit rusting. The carbonic acid and electrolytic theories are inferred from the circumstance that all alkalis inhibit rusting, but both theories are disproved by direct experimental evidence which cannot be disregarded. Beyond this, however, these theories make no serious attempt to explain the inhibiting action of other agents, such as chromic acid and its potassium salts, potassium iodate, permanganate, and ferrocyanide, and hydrogen peroxide. The action of chromic acid is no doubt to be ascribed to its rendering the iron passive, but no explanation has been advanced so far to explain the action of other inhibiting agents.

On the other hand, the suggestion that hydrogen peroxide is concerned has been much more successful as a working hypothesis in affording, at any rate, some reason for the action of the inhibiting agents, and in suggesting new lines of work. But here also the explanation is not wholly satisfactory or complete, since it now appears that there are some substances which decompose hydrogen peroxide, but do not inhibit rusting.

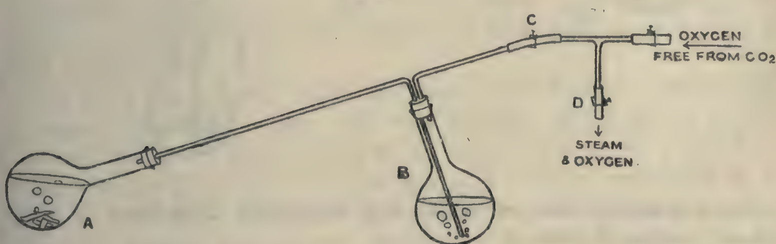
The action of the inhibiting agents is therefore a stumbling-block to any complete explanation of rusting. It is one of the main objects of this paper to throw further light on this question, and it will be shown that all inhibiting agents owe their action to the same cause, which differs from that ascribed to them by any of the explanations so far suggested.

Experimental.

The Solubility of Iron in Water.

Before proceeding to a consideration of this subject, it is necessary to record the results of further experiments designed to test the applicability of the electrolytic theory, a subject which has been discussed in a previous paper. In addition to the results then presented, the following experiment was devised in order to deter-

Fig. 1.



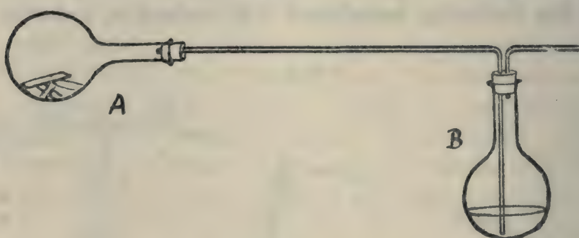
mine whether experimental evidence could be found for the assumed production of ferrous ions.

A and *B* were round Jena-glass flasks fitted with rubber stoppers and delivery tubes as shown. One of the delivery tubes from *B* was connected to a T-piece, one limb of which was open to the air and the other connected to an apparatus for supplying oxygen free from carbon dioxide. The flasks were three parts filled with distilled water, which was then boiled vigorously for some time. The steam from *A* escaped through *B* to the outlet in the T-piece. After boiling for a considerable time, the stopper of *A* was removed, and some bright strips of very pure iron * were quickly dropped into the boiling water. The stopper was then replaced as quickly as possible. The boiling was continued for a quarter of an hour longer, and during the whole time a current of oxygen free from carbon dioxide was being passed through the outlet of the T-piece

* The iron used in the experiments described in this and in the paper on the "Passivity of Iron and certain other Metals" was highly purified sheet iron. Sheet iron prepared by electrolysis behaved in a similar manner.

along with the steam. At the end of a quarter of an hour the flask *A* was allowed to cool, and became completely filled with boiling water from *B*. The water in *B* was boiled for a short time longer, and then the clip *C* was tightly screwed up. When the water in *A* and *B* had become quite cold, *D* was screwed up, thus stopping the exit of the oxygen. The clip *C* was then again unscrewed carefully, and a slow current of oxygen free from carbon dioxide drawn into *B*. When *B* was full of oxygen, the delivery tube, which had been drawn out at one point, was sealed. The stoppers were flooded with paraffin wax, and the apparatus fixed up in such a position that the delivery tube between *A* and *B* was horizontal, thus:

FIG. 2.



The apparatus was set aside, and examined from time to time for any signs of rust.

If the iron in *A* passes into solution in the water, as is assumed by the electrolytic theory, the ferrous ions so produced will diffuse from the flask *A* along the delivery tube towards *B*. Dissolved oxygen will at the same time be diffusing from *B* towards *A*; thus if the tube between *A* and *B* be sufficiently long, the ferrous ions should meet the dissolved oxygen, and produce rust somewhere in the tube. The length of the tube was 14 inches, and it was of narrow bore. Since no rust was visible in the flask *A* or in the tube after several months, it can be assumed that the oxygen was not diffusing towards *A* too rapidly. After six months the iron in *A* began to tarnish, and slowly developed a green film over the entire surface. After eight months the iron was completely and uniformly covered with an adherent green film, due to the formation of ferrous hydroxide along with a little ferric hydroxide, a mixture well known to produce a green colour. There was no sign of rust anywhere else in the flask or in the tube. From this it may safely be concluded that iron cannot rust until the oxygen actually reaches its surface, and that rusting in the absence of any acid is not preceded by solution of iron in the water.

Objections to the Electrolytic Theory.

The result of the above experiment confirms those previously recorded, and is in direct opposition to any theory which requires that the iron should pass into solution before forming rust. There are, however, many other objections to the electrolytic theory which it is convenient to enumerate here.

I. If iron passes into solution in pure water, the ferrous ions and the hydroxyl ions should form ferrous hydroxide, and hydrogen should be liberated. The process should be continuous, and appreciable amounts of these products should be formed. This, however, is not the case, as iron may be immersed in pure water for months without any change taking place. The upholders of the theory explain this fact away by assuming that the iron becomes polarised by the hydrogen which is liberated, thus stopping the action in its early stages; that on access of oxygen the latter acts as a depolariser, removing the film of hydrogen, and then only the process becomes continuous. There are four definite objections to this explanation:

(*a*) It is improbable that the iron could become permanently polarised until the water and the vacuous space above it had become saturated with hydrogen, in which case there would be a sufficient quantity both of hydrogen and ferrous hydroxide to be readily detected. Also iron can remain in boiling water for considerable periods without any apparent action taking place; and it is extremely improbable that under these conditions a complete film of hydrogen could be maintained unreplenished.

(*b*) There is no evidence to show that dissolved oxygen can oxidise free hydrogen directly. The iron cannot facilitate this, since it is assumed to be kept out of contact with the water by the hydrogen film.

(*c*) If dissolved oxygen is able to depolarise the iron, other depolarising agents, such as potassium dichromate, chlorate, and nitrate, should effect the same result. This, however, is not the case.

(*d*) If iron can be polarised by the small concentration of hydrogen ions present in pure water, it should be at least equally polarised by a weak solution of carbon dioxide, since it is to be expected that the effect will be increased by raising the concentration of the hydrogen ions. This, however, is not the case. Many objections therefore arise to the supposition that iron becomes polarised in pure water.

II. Very dilute alkaline solutions allow copious rusting to occur, although their solutions are effective in fixing carbon dioxide. For

example, in presence of a solution of baryta (0·007 per cent.) iron will rust as copiously as it does in pure water with access of air freed from carbon dioxide. The concentration of hydroxyl ions in this solution is $6{\cdot}5 \times 10^{-4}$. Assuming the concentration of the hydrogen ions and of the hydroxyl ions in pure water to be $1{\cdot}0 \times 10^{-7}$, the product of the two is $1{\cdot}0 \times 10^{-14}$. This product must remain constant, so that when the concentration of the hydroxyl ions is increased from 10^{-7} to $6{\cdot}5 \times 10^{-4}$, which is the case in the 0·007 per cent. baryta solution, the concentration of the hydrogen ions will fall from 10^{-7} to $1{\cdot}538 \times 10^{-11}$. Thus the concentration of the hydrogen ions in the 0·007 per cent. baryta solution is 1/6500th of the concentration in pure water. According to the electrolytic theory, this enormous lowering of the concentration of the hydrogen ions should reduce any possible rusting to a negligible quantity. This is not the case, for, on the contrary, copious rusting occurs, and similar results are obtained with dilute solutions of other alkalis.

III. As will be shown later, the aerial oxidation of copper resembles that of iron. The electrolytic theory might therefore be expected to apply to the case of copper, and, indeed, of all metals. The electrolytic solution pressure of copper is 10^{-12} atmosphere, a value much smaller than that of hydrogen, which is 10^{-4} atmosphere. Consequently, no copper ions could replace the hydrogen ions in pure water, and thus pass into solution. According to the electrolytic theory, therefore, no oxidation should take place when copper is immersed in distilled water exposed to the air. This, however, is not the case, for copper does slowly oxidise in these circumstances.

IV. The electrolytic theory does not explain the action of the various inhibiting agents other than the alkalis; such as, for example, potassium chromate, and dichromate, iodate, ferrocyanide, and hydrogen peroxide. All these agents inhibit rusting, but according to the electrolytic theory most of these substances should assist it by depolarising the iron.

These are some of the difficulties which prevent the acceptance of the electrolytic theory as an adequate explanation of the rusting of iron, even if the fundamental fact of the solution of iron in pure water were proved to be correct.

Tilden describes an experiment in which water is repeatedly distilled from solid baryta on to iron contained in a silica boat in a vacuum. This experiment has been repeated by us with the same result, namely, the iron became coated with a thin film of oxide after water had been distilled on to it about twenty times and evaporated off again. The film, however, was confined entirely to

the surface of the iron, and none could be observed on the silica boat. This fact is an indication that the oxide was not deposited from solution, but was actually formed on the surface of the iron. This is no doubt due to the presence of a trace of oxygen. Minute quantities of air were probably retained by the baryta crystals. The crystals break up to an amorphous powder on repeatedly heating, and would thus allow of the escape of any air which had been occluded or enclosed. Most soluble crystalline substances disengage air when dissolved in water in a vacuum. The conditions of this experiment ensure the complete absence of carbon dioxide, but not of oxygen.

Tilden also calls attention to the fact that ferrous hydroxide is the first product in the rusting of iron. The following experiment also leads to the same conclusion which has been accepted in the previous papers.

A strip of iron was dropped into boiling water contained in a round Jena-glass flask. After continuing the boiling for a few minutes the flask was sealed and allowed to cool. When cold, air free from carbon dioxide was admitted. There was no change visible for about an hour, and then a white cloudiness began to form on the surface of the iron. This was evidently finely divided ferrous hydroxide; it was rapidly carried away from the iron by convection currents forming white streams in the water. This ferrous hydroxide was obviously formed at the surface of the iron, and afterwards carried out into the water. It did not make its appearance until the air had diffused down from the surface of the water and reached the iron. It was obviously extremely finely divided, being carried about by convection currents very readily. It was not for some hours that the ordinary yellow colour of rust made its appearance.

The Cause of the Action of the Inhibiting Agents.

As previously pointed out, any complete theory of rusting must include an explanation of the action of those substances which inhibit the process. During the course of this investigation it was found that, in addition to chromic acid and the chromates, many other agents also rendered iron passive, amongst them the alkalis. It was eventually found that all agents which inhibit rusting also render iron passive, and, further, that the inhibition of rusting is a direct result of the passive condition of the iron.

The following were the tests employed for showing the passivity of the iron:

(1) A solution of nitric acid of specific gravity 1·2.

(2) A dilute solution of copper sulphate. A strength of 0·5 per cent. was found to be the most suitable.

(3) Immersion of the iron in distilled water, and observation of the time elapsing before rusting begins.

Of these tests the copper sulphate solution proved to be the most convenient.

With regard to the method of testing employed, some precautions are necessary in washing the iron and immersing it in the testing liquid. It must be washed with distilled water, and must not be touched with the hands or shaken too violently, since such action tends to destroy passivity. Perhaps the best method is to remove the iron from the solution by means of a very thin glass rod, bent into a hook at one end. The hook is inserted in a hole previously bored in the sheet of iron. The iron is quickly dipped two or three times in distilled water, and then immersed in the testing liquid and the rod removed.

A simpler method is to pour off the solution, and rinse out the vessel (a gas-jar is the most convenient) several times with distilled water. The testing liquid is then quickly poured over the iron so as completely to cover it. The whole process should be done as rapidly as possible, and without unduly shaking the iron.

Nitric acid of specific gravity 1·2 attacks active iron at once with effervescence and the formation of a brown solution. Passive iron is not so attacked, and will remain perfectly bright and unacted on for times varying from a few seconds to several hours. It is at once attacked, however, if touched with a piece of active iron or scratched with a sharp glass rod. The action visibly spreads from the point so touched over the whole surface.

Copper sulphate solution (0·5 per cent.) at once deposits a film of copper on active iron. Passive iron will remain in the solution sometimes for hours quite unaffected and perfectly bright. It becomes active, however, if touched with a piece of active iron or scratched with a glass rod, and the film of copper can be seen spreading from the point over the entire surface.

In distilled water exposed to the atmosphere, active iron usually begins to rust visibly in eight to ten minutes. Passive iron will sometimes remain perfectly bright for one to two hours before rusting begins, and then the action is very local for a considerable time. The most uniform results are given with iron which has been etched with nitric acid (D 1·2).

Passivity induced by Agents which Inhibit Rusting.

Chromic Acid:—Various strengths of chromic acid were employed, and the duration of the immersion was usually from eighteen hours to several days.

It was found that 1, 0·5, 0·1, 0·05, and 0·025 per cent. solutions of chromic anhydride rendered iron passive to nitric acid (D 1·2), the weaker solutions requiring a longer immersion up to four or five days. After prolonged immersion, iron was rendered slightly passive, even by a 0·01 per cent. solution of chromium trioxide. Iron which had been treated with 1 per cent. chromium trioxide remained passive to nitric acid (D 1·2) for several hours. In copper sulphate solution, iron which had been immersed in 1 per cent. chromium trioxide overnight remained unacted on for five hours. In distilled water exposed to the atmosphere, iron which had been immersed in 1 per cent. chromium trioxide for one day remained unattacked for considerable periods varying from one to two hours, and sometimes more. Rusting was only very local after four hours. In the blank test with active iron in distilled water, rusting began in ten minutes, and was copious in fifteen minutes.

The chromic acid used in these experiments was specially purified, and no sulphuric acid or nitric acid could be detected in it.

One per cent. Solution of Potassium Dichromate:—Pieces of iron, some with etched and some with unetched surfaces, were immersed in 1 per cent. dichromate for several days. On testing with nitric acid (D 1·2) they remained unattacked for times varying from a few seconds to several minutes.

Iron which had been immersed in 1 per cent. dichromate for two days was passive to 0·5 per cent. copper sulphate solution for twelve minutes. Iron was immersed for one day in 1 per cent. dichromate; it was then washed, and left in distilled water. There was no rusting after one and a-half hours, and only local rusting in four hours.

One per cent. Solution of Potassium Chromate:—Sheets of iron with etched surfaces were immersed in 1 per cent. potassium chromate for several days. They were then tested with nitric acid (D 1·2), and found to be passive for times varying from one minute to a few seconds.

Immersion for several days in 1 per cent. potassium chromate rendered iron passive to 0·5 per cent. copper sulphate solution, in which it remained unacted on for five hours.

Iron which had been treated with 1 per cent. potassium chromate for one day was immersed in distilled water, and showed no rusting for more than an hour.

Potassium Chlorate:—In a 1 per cent. solution iron rusted readily, and it remained active, as shown by all the three tests. In a 4 per cent. solution there was no rusting, and after a two days' immersion the iron was found to be passive to nitric acid (D 1·2) and to 0·5 per cent. copper sulphate. In distilled water, however, rusting began almost as quickly as in a blank test with active iron.

Potassium Bromate:—A 1 per cent. solution allowed slight incipient rusting. This soon stopped, and most of the surface remained bright. On testing the iron with nitric acid (D 1·2) (after an immersion of one day in the potassium bromate) it was found to be passive.

Another sheet of iron which had been immersed for two days in 1 per cent. potassium bromate was passive to 0·5 per cent. copper sulphate, and remained so for five minutes.

After treatment with the potassium bromate solution for one day a sheet of iron showed slight local oxidation. On washing and immersing in distilled water no additional rusting had occurred after one and three-quarter hours, and only very little in four hours.

Potassium Iodate:—In a 1 per cent. solution iron usually remained unrusted. Several sheets of iron were treated for one or two days, and were then tested for passivity. One sheet was unacted on by nitric acid (D 1·2), another remained unacted on by 0·5 per cent. copper sulphate solution for three minutes, and a third on washing and immersing in distilled water did not begin to rust for fifty minutes.

Potassium Permanganate:—A sheet of iron which had been lying in 0·5 per cent. potassium permanganate solution for several weeks showed no rusting, although it had assumed a yellow colour owing to a thin film of manganese dioxide which had formed on it. On washing and immersing in nitric acid (D 1·2) the film of manganese dioxide was dissolved away, leaving the bright surface of the iron exposed. The iron remained unacted on for several hours, and was therefore passive.

Sodium Arsenate:—A 1 per cent. solution allowed a little local rusting to occur. This soon stopped, and most of the surface remained bright. On immersing in nitric acid (D 1·2) the green patch of rust slowly dissolved, leaving the bright iron surface quite unacted on.

Hydrogen Peroxide:—In a 1 per cent. solution (made from "Perhydrol," and quite free from acid) a smooth sheet of iron did not rust at all, but oxygen was continuously disengaged at the

surface of the iron. After immersion in the hydrogen peroxide solution for two days the iron was passive to nitric acid (D 1·2).

Potassium Hydroxide:—After immersion in 1 per cent. potassium hydroxide for twelve hours iron was found to be passive to nitric acid (D 1·2). Another sheet of iron, similarly treated, was passive to 0·5 per cent. copper sulphate solution, and remained unacted on for five hours.

Bright sheets of iron which had been immersed in 1 per cent. potassium hydroxide for one or two days did not begin rusting in distilled water for times varying from half an hour to one hour. In a blank experiment iron began to rust copiously in eight minutes.

Barium Hydroxide:—A solution of 1 per cent. baryta had the same effect as 1 per cent. potassium hydroxide.

Sodium Carbonate:—After being immersed for eighteen hours in 1 per cent. sodium carbonate the iron was passive to nitric acid (D 1·2). Also iron which had been kept for four months in solutions of 0·14 and 0·13 per cent. sodium carbonate and of 0·2, 0·15, and 0·14 per cent. potassium carbonate and had remained quite bright, was in every case passive to nitric acid (D 1·2).

After an immersion of eighteen hours in 1 per cent. sodium carbonate, iron was passive to copper sulphate solution, remaining unacted on for five hours.

Iron was treated with 1 per cent. sodium carbonate for three days, then washed thoroughly, and immersed in distilled water. Rusting did not begin for forty-five minutes. On repeating the experiment, rusting began very locally in half an hour. Blank tests were made at the same time, in which the active iron showed general rusting in eight minutes.

Borax:—After immersion overnight in 1 per cent. borax solution, iron was passive to nitric acid (D 1·2) for one minute. Another piece of iron which had been immersed in 1 per cent. borax for two days was passive to copper sulphate solution for five minutes. Iron with an etched surface was immersed in 1 per cent. borax for three days. It was then washed, and left in distilled water. No rusting was visible for an hour and a-half. A similar piece of active iron showed rusting in ten minutes.

Ammonia:—After immersion for two days in ammonia solution (D 0·880) iron was passive to nitric acid (D 1·2) for half a minute. Another piece of iron similarly treated was passive to copper sulphate solution, no action taking place for ten minutes.

Potassium Ferrocyanide:—Strips of iron were immersed in 1 per cent. potassium ferrocyanide solution for one day.

One piece on testing with nitric acid (D 1·2) was found to be passive. Another piece was tested with copper sulphate solution, and remained unacted on for one minute. A third piece was immersed in distilled water after carefully washing it. Rusting began very locally in half an hour, and there was still very little after an hour. A blank test showed general rusting in eight minutes.

Reference to the following table will show that in the case of solutions which do not inhibit the rusting of iron, such as sodium chloride, sodium sulphate, etc., no passivity of the iron was induced.

Tabulated Results of Experiments on the Production of Passivity by Various Solutions.

Solution.	Strength. Per cent.	Resulting state of iron in: Nitric acid (D 1·2)	0·5 per cent. $CuSO_4$.	Distilled water.	Whether solution inhibits or allows rusting.
Chromic acid	0·01 to 1	Passive	Passive	Passive	Inhibits
Potassium dichromate	1	Passive	Passive	Passive	Inhibits
Potassium chromate	1	Passive	Passive	Passive	Inhibits
Potassium chlorate	1	Active	Active	Active	Allows
Potassium bromate	1	Passive	Passive	Passive	Passive
Potassium iodate	1	Passive	Passive	Passive	Inhibits
Potassium permanganate	0·5	Passive			Inhibits
Sodium arsenate	1	Passive			Inhibits after slight initial action
Hydrogen peroxide	1	Passive			Inhibits
Potassium hydroxide	1	Passive	Passive	Passive	Inhibits
Barium hydroxide	1	Passive	Passive	Passive	Inhibits
Sodium carbonate	1	Passive	Passive	Passive	Inhibits
Sodium carbonate	0·13	Passive			Inhibits
Potassium carbonate	0·14	Passive			Inhibits
Borax	1	Passive	Passive	Passive	Inhibits
Ammonia	D 0·880	Passive	Passive		Inhibits
Sodium chloride	1	Active	Active	Active	Allows
Sodium sulphate	1	Active	Active	Active	Allows
Potassium nitrate	2	Active	Active		Allows
Potassium iodide	1	Active	Active		Allows
Potassium chlorate	4	Passive	Passive		Inhibits
Potassium ferrocyanide	1	Passive	Passive	Passive	Inhibits

From the above table it is evident that all those agents which inhibit rusting rendered iron passive, whilst those which allowed rusting did not render it passive. Not a single exception was found to this rule. The inference may therefore be drawn that the chromates, alkalis, and other inhibiting agents owe their action in preventing rusting to the fact that they all render iron passive to a greater or less extent.

That iron cannot rust so long as it is in the passive state was shown by the following experiment:

Four sheets of iron were immersed in 1 per cent. chromic acid for two days in separate vessels. They were thoroughly washed, and left to stand in distilled water. After one and a-half hours one of the pieces began to rust. It was tested with nitric acid (D 1·2), and found to be active. The other three which had remained perfectly bright were also tested, and found to be still passive to nitric acid (D 1·2). Thus, one of the pieces of iron had become active, and consequently rusted; the other three remained passive, and had therefore not rusted.

The fact that alkalis are capable, even when quite dilute, of rendering iron passive appears at first sight to be rather a startling one. But it has long been known that iron becomes passive in fused alkalis, and more recently several experimenters have shown that iron electrodes can be rendered passive in alkaline solution by passage of the electric current (P. Krassa, *Zeitsch. Elektrochem.*, 1909, **15**, 490).

Two of the tests—the nitric acid (D 1·2) and the copper sulphate tests—showed that the alkalis act even more powerfully in this respect than potassium chromate and dichromate. In the case of the third test, namely, the rusting in distilled water, iron which had been rendered passive by alkalis did not appear to retain its passivity quite so long as iron similarly treated with the chromates. But when a control experiment with active iron is employed there can be no doubt whatever that the iron which has been treated with alkali has become passive, since it remains bright long after the iron used as the control has copiously rusted.

It should be added that dilute acids, including carbonic acid, as well as many salts, destroy more or less rapidly the passivity of iron. On any of the several theories as to the cause of the passivity of iron it is difficult to understand the passive effect induced by alkalis. It is not established that dilute alkaline solutions can induce the oxidation of iron and form a film of oxide on the surface. In fact, it is clear that the long-standing problem of the passivity of iron has not yet received complete explanation.

Passivity and Rusting.

The demonstration of the intimate connexion between the inhibition of the rusting of iron and its passivity renders a new theory of rusting necessary. The carbonic acid and the electrolytic theories depend largely on the fact that alkalis inhibit rusting; and since this phenomenon has now been explained in another way, these theories have lost the main support which justified their existence, besides being opposed to other facts alluded to above.

The fact that alkalis render iron passive negatives the conclusions

recorded in a paper published recently in support of the carbon dioxide or acid theory of rusting (Friend, *J. Iron Steel Inst.*, 1908, II, 5). In a series of experiments in which water was distilled on to iron in presence of air free from carbon dioxide, the iron was in some cases previously immersed in potassium hydroxide, and in others not. In all the experiments where the iron had been treated with potassium hydroxide it did not rust, but it did so when not previously so treated. The explanation given was that when the iron did not rust there was no carbon dioxide present; but when it did rust there was carbon dioxide present on the surface of the iron or glass, since these had not been immersed in potassium hydroxide. This is assumed to be so from the green colour of the rust characteristic of ferrous carbonate. The true explanation is that the iron did not rust because it had been rendered passive by the potassium hydroxide, whilst when not so rendered passive the iron did rust, in spite of the absence of carbon dioxide. The green colour of the rust was obviously the well-known colour of ferrous hydroxide containing a little ferric hydroxide.

Some of the results published by Moody in support of the carbonic acid theory now receive a different explanation. After treatment of iron with chromic acid and subsequent exposure to the action of water and air free from carbonic acid, the iron was found not to rust. The explanation is that it had been rendered passive by the chromic acid.

Iron which has been rendered passive by chromic acid will remain unrusted in presence of water and air free from carbon dioxide for long periods. The access of carbon dioxide destroys the passivity, and rusting ensues.

It was pointed out previously in discussing the electrolytic theory that very dilute alkalis allow rusting to take place readily, although the concentration of the hydroxyl ions is overwhelmingly greater than that of the hydrogen ions of the water. According to the electrolytic theory this should not be so.

The phenomenon can, however, be very satisfactorily explained by the fact that alkalis below a certain dilution are not capable of rendering iron passive. Support is given to this view by some experiments which were carried out on the limiting concentration of alkalis just necessary to prevent rusting. It was found that 0·13 per cent. sodium carbonate and 0·14 per cent. potassium carbonate prevented rusting, and after immersion for four months the iron was found to be passive to nitric acid (D 1·2). With weaker solutions rusting occurred and the iron remained active. Similar results were obtained with dilute barium and sodium hydroxide solutions. An immersion of a few minutes in

the various reagents is often sufficient to effect the passivity of the iron.

Comparison of the Oxidation of Iron with that of Other Metals.

The respects in which the rusting of iron differs from the oxidation of other metals may now be considered. The following appear to be the principal differences:

(1) The rusting of iron is usually more continuous and deep-seated than that of most other metals; it produces pitting and a more rapid waste of the metal.

This has been ascribed to the fact that the oxides of the other metals are more coherent, and therefore more protective, than that of iron, and also to the fact that metallic iron is usually less pure than other metals, thus promoting electrolytic action. Lead is a good example of a metal which protects itself by means of a film of oxide. A bright surface of lead, however, begins to oxidise much sooner than a bright surface of iron. In distilled water lead shows visible oxidation in one or two minutes, whilst iron does not do so for seven or eight minutes. It therefore seems probable that this peculiarity of iron is not due to any fundamental difference in the chemical reaction of oxidation.

(2) The rusting of iron being inhibited by a large number of agents, the question arises as to whether other metals are similarly protected by all or some of these agents.

(3) Lastly, it is stated that hydrogen peroxide cannot be detected during the rusting of iron, whilst it can be detected during the rusting of other metals.

Apart from these three points the oxidation of iron does not appear to differ in any material way from that of other metals.

The table on p. 1850 summarises the results of experiments on the effect of various solutions on the oxidation of zinc, copper, aluminium, magnesium, and iron, and it may be added that the aerial oxidation of lead is inhibited by alkalis and by other of the agents mentioned which do not directly attack the metal.

It will be seen from this table that chromic acid inhibits metallic oxidation in all cases where the acid has no direct action on the metal. Potassium dichromate and chromate inhibit the oxidation of all the five metals. Sodium carbonate and borax inhibit the oxidation of iron, zinc, and copper, and allow an action in the case of aluminium and magnesium.

Potassium hydroxide appears to have a direct action on all the metals examined except iron. Potassium iodide allows oxidation of all the metals, and this is also the case with the chlorides, nitrates, and sulphates of the alkali metals, although they have

Solution.	Iron.	Zinc.	Copper.	Aluminium.	Magnesium.
Chromic acid	Inhibits	0·1% inhibits. 1% acts on the metal	Inhibits	Inhibits	Acts on the metal
Potassium dichromate	Inhibits	Inhibits	Inhibits	Inhibits	Inhibits
Potassium chromate	Inhibits	Inhibits	Inhibits	Inhibits	Inhibits
Sodium carbonate	Inhibits	2% inhibits. 1% allows some action	5% inhibits. Stronger solutions act on the metal	Acts on the metal with evolution of hydrogen	Allows
Borax	Inhibits	1% inhibits	Inhibits	Retards	Allows
Potassium hydroxide	Inhibits	1% inhibits. Stronger solutions have a direct action	Allows	Acts on the metal with evolution of hydrogen	Acts on the metal with evolution of hydrogen
Potassium iodide	Allows	Allows	—	Allows	Allows
Potassium iodate	Inhibits	Allows	Acts on the metal producing blackening	Inhibits	Acts on the metal
Potassium bromate	Inhibits (after slight initial action).	Allows (acts on the metal)	—	—	—
Potassium ferrocyanide	Inhibits	Inhibits	Produces film on the metal	Inhibits	Allows
Potassium ferrocyanide	Allows	Allows	Produces film on the metal	Allows	Allows

not been included on the list. Potassium iodate only inhibits in the case of iron and aluminium. Potassium ferrocyanide inhibits the oxidation of iron, zinc, and aluminium, whilst potassium ferricyanide allows an action with all the five metals.

It is thus evident that these various solutions exert an influence on the aerial oxidation of zinc, copper, aluminium, and magnesium very similar to that produced on the oxidation of iron. Especially is this true of the chromates. It has also been found that potassium bichromate and chromate render these metals passive just as they render iron passive.

The Production of Hydrogen Peroxide during the Rusting of Iron.

Direct proof that hydrogen peroxide is formed when iron rusts has not hitherto been available. Keiser and McMaster (*Amer. Chem. J.*, 1908, **39**, 96), in testing for minute quantities of hydrogen peroxide, employed a mixture of potassium ferricyanide and ferric chloride solutions. They found this to be the most delicate reagent

of a large number which they tried. The potassium ferricyanide is acted on by hydrogen peroxide, giving ferrocyanide, which produces a coloration with the ferric chloride.

It was thought that this reagent might prove useful in testing for hydrogen peroxide during the oxidation of metals. On comparing its delicacy with that of titanic acid, it was found to be possible to detect hydrogen peroxide in a solution six times as dilute as one which just gave a yellow colour with titanic acid. The strength of these solutions was estimated, and it was concluded that one part of hydrogen peroxide in 200,000 parts of water could be detected by the ferricyanide reagent. A blank experiment must always be done at the same time, and the reagent must be freshly prepared and fairly dilute so as not to have too deep a colour.

This test was now applied to the oxidation of metals. The water in which zinc, lead, magnesium, and aluminium had been oxidising for a considerable time was tested. In every case the reagent turned green after remaining a short time, eventually becoming a very deep green and sometimes of a blue colour, thus showing the presence of hydrogen peroxide. Zinc and aluminium gave the strongest reactions.

Attention was now turned to iron. Some bright sheets of a highly purified soft iron were allowed to rust in distilled water, and the latter was tested from time to time for hydrogen peroxide. In order to make sure that no coloration of the reagent was caused by the presence of iron in solution, three parallel tests were employed; in addition to the actual test and the blank test with distilled water, a third test was made with ferricyanide to show whether there were any iron in solution. This last test almost invariably showed no coloration, and this showed that the results were not vitiated by the possible presence of iron in solution.

On the first day after the iron had been immersed no hydrogen peroxide could be detected in the water. On the second day, however, there was a slight reaction, and on the third day a pronounced reaction for hydrogen peroxide. Strong reactions continued to be given for about a fortnight, when they began to diminish, and eventually disappeared altogether. The strongest reactions obtained were quite comparable to those with lead and magnesium. On repetition of this experiment the same results were obtained, the presence of hydrogen peroxide usually lasting for a week or a fortnight, and finally disappearing. The eventual disappearance of the peroxide may be due to the formation of some ferrous hydroxide which would destroy it.

Thus in the case of iron a small quantity of hydrogen peroxide is formed during oxidation, just as with the other metals. The precise

significance of the formation of hydrogen peroxide during the aerial oxidation of metals has not yet been discovered.

Conclusions.

None of the existing theories adequately explains how the various inhibiting agents prevent rusting. A satisfactory explanation, however, is provided by the fact that all these agents, without exception, render iron passive, and that this passivity persists after removal from the solution which caused it. Iron, so long as it is passive, does not rust in presence of oxygen and water. If exposed to atmospheric air, passive iron very gradually rusts, owing to the removal of the passivity of the iron by the carbon dioxide of the air. Passivity of metals may vary in amount, and the amount of rusting subsequently induced will depend on the extent to which this passivity is removed. The nature of passivity will be dealt with in another paper.

The mechanism of the process of the rusting of iron does not appear to differ essentially from the aerial oxidation of other metals. Similar reagents inhibit in all cases, and traces of hydrogen peroxide can be detected when iron rusts, just as in the case of the other metals. All the metals concerned will, however, readily oxidise in solutions of potassium iodide, and in certain other reducing agents which render the existence of hydrogen peroxide impossible. Consequently, the hydrogen peroxide is probably not an intermediate product of the main reaction, but may be the result of a secondary reaction, since the process of oxidation can apparently continue without its formation.

We consider, therefore, that metals undergo aerial oxidation by direct action of oxygen dissolved in water. In the case of iron, ferrous hydroxide is first produced, and is afterwards further oxidised to the ferric state, forming rust. Iron does not pass into solution before rust can be formed. The action of carbonic acid or of any other acid is separate and independent of the main process of rusting, which proceeds in their absence.

Several experiments which have been recently recorded as affording support to the old view that carbonic acid is necessary for the rusting of iron are explained by the results now recorded. The fact that iron which has been treated with dilute chromic acid or other inhibiting agents and subsequently washed, does not rust in air free from carbon dioxide, but begins to rust after carbon dioxide has been admitted, is due to the destruction of the passivity of the iron through the action of carbon dioxide.

A similar explanation can be given of an experiment recorded by Friend (Proc., 1910, **26**, 179), and intended as a lecture

experiment to demonstrate the necessity of carbonic acid for the rusting of iron. In this apparatus a hollow iron cylinder previously immersed in potassium hydroxide solution is shown afterwards not to rust in presence of water and air free from carbon dioxide. This result is due to the passivity of iron induced by the alkali, and does not prove, as is assumed, that iron cannot rust unless carbon dioxide is present. If carbon dioxide is admitted, the passivity of the iron is destroyed, and rusting proceeds (see also Dunstan, *Nature*, 1911, p. 381).

SCIENTIFIC DEPARTMENT,
IMPERIAL INSTITUTE.

CCIX.—*The Passivity of Iron and Certain Other Metals.*

By WYNDHAM ROWLAND DUNSTAN and JOHN RICHARD HILL.

THE evidence presented in the foregoing paper shows that the problems of passivity and the rusting of iron are closely connected. During the course of that investigation some new facts were brought to light which led to further experiments being made with regard to the passivity of both iron and other metals.

Of the numerous theories which have been put forward from time to time to explain the well known passive state of iron, not one can be said to have accounted successfully for all the observed phenomena. Most of these theories agree that passivity is caused by the formation of an extremely thin protective film on the surface of the metal. The protective film may possibly be composed of the metal itself, the surface of which has assumed some abnormal condition. Such a view is held by Hittorf, who considers that passivity is due to a state of electric tension on the surface of the metal (*Zeitsch. physikal. Chem.*, 1900, **34**, 385). Finkelstein expresses the opinion that the surface layer of the iron has been changed from the bivalent to the tervalent state (*Zeitsch. physikal. Chem.*, 1901, **39**, 91).

Then the protective film may also be of a non-metallic nature—either solid or gaseous. Fredenhagen believes it to be a film of oxygen in a condensed condition (*Zeitsch. physikal. Chem.*, 1903, **43**, 1; 1908, **63**, 1). Krassa (*Zeitsch. Elektrochem.*, 1909, **15**, 490) and many others adhere to the theory that passive iron is covered with a film of oxide—probably the magnetic oxide. This

is perhaps the theory which has received the most general support. Heathcote has summarised the facts at considerable length (*J. Soc. Chem. Ind.*, 1907, **26**, 899), and draws the conclusion that none of the theories is satisfactory, but that the oxide theory has most in its favour. A similar view is held by Byers (*J. Amer. Chem. Soc.*, 1908, **30**, 1718). The oxide film, if it exists, must be exceedingly thin, since it does not appear to affect the colour of the metal or to diminish its reflecting power. Müller and Königsberger (*Zeitsch. Elektrochem.*, 1907, **15**, 659) performed experiments with iron mirrors, and could find no constant difference in the reflective power after rendering the iron passive. Krassa states that a film of oxide thick enough to produce passivity would not change the reflective power more than 2 per cent., and would therefore escape detection. Müller and Königsberger, however, deny this.

Krassa also gives an account of some work on the production of passivity of iron in alkali solutions by anodic polarisation. In boiling alkalis the passive state was quickly attained with strong currents, producing no visible alteration of the surface. With weak currents, however, a visible film of oxide was first produced, and this attained a considerable thickness before passivity was eventually arrived at. He attributed these results to the fact that with strong currents a complete, although thin, film of oxide was rapidly formed, whilst with weak currents the film was more irregular, and consequently attained a much greater thickness before becoming complete. Krassa considers that oxide is formed by direct electrolytic action of the alkali on iron with the liberation of hydrogen, the amount of hydrogen formed being usually too small to be detected.

It has been previously supposed that the passive state is confined to a very few metals, chiefly iron, nickel, and cobalt. It will be shown now, however, that other metals also exhibit passivity.

The Passivity of Iron.

As pointed out in the foregoing paper, all the solutions which inhibit rusting also render iron passive. The principal solutions are: chromic acid, potassium dichromate, chromate, permanganate, iodate, bromate, chlorate, and ferrocyanide, hydrogen peroxide, hydroxides of potassium, sodium, calcium, barium and ammonium, carbonates of sodium and potassium, and borax

An immersion of a few minutes in one of these solutions is often sufficient to effect passivity. An account was given in the previous paper of the precautions to be taken in washing the iron and of the methods employed for detecting the passive state. The three tests were: nitric acid (D 1·2), a solution of copper sulphate (0·5 per cent.), and rusting in distilled water. As indicated in the fore-

going paper, the iron used in these experiments was wrought iron sheet of a high degree of purity, whilst sheet iron prepared by electrolysis furnished the same results.

Influence of Air on Production of Passivity.

That passivity is produced in the absence of air was shown in several ways:

(1) Iron was immersed in boiling 1 per cent. solutions of chromic acid, potassium dichromate, sodium carbonate, and potassium hydroxide for several hours. In every case the iron was found to be passive to nitric acid (D 1·2) after this treatment.

(2) Iron was dropped into a boiling 1 per cent. solution of sodium carbonate contained in a flask. The flask was sealed while boiling, and allowed to cool. After twenty-four hours the flask was opened, and the iron was found to be passive on testing with nitric acid (D 1·2). The experiment was also made with 1 per cent. solutions of chromic acid and potassium bromate, both of which gave the same result.

(3) Some iron was placed in one limb of a bent tube and a 3 per cent. solution of potassium hydroxide in the other. The tube was connected with a Sprengel pump and completely evacuated, the potassium hydroxide being finally boiled to drive out all dissolved air. The tube was then sealed, and the alkali run over on to the iron, where it was allowed to remain overnight. The alkali was then poured back again, and the iron washed repeatedly by distilling water over from the alkali. Finally, the tube was carefully opened, the iron tested with copper sulphate solution, and found to be passive.

Thus, in all these cases air plays no part in rendering iron passive.

Destruction of Passivity.

When iron which had been rendered passive by chromic acid was washed and immersed in distilled water, it usually remained passive for upwards of an hour. Eventually, however, it slowly became active, and rusting began. This action was due to the carbonic acid from the air which destroyed the passivity. This was shown to be so by an experiment in which carbon dioxide was rigorously excluded, and the iron protected from contact with the glass by means of a silica boat. In this case no rusting had occurred after several months. When the iron had not been previously rendered passive, rusting occurred as usual.

The passivity was not destroyed in distilled water by touching the iron with zinc or active iron. It was, however, thus destroyed

when immersed in copper sulphate solution or in nitric acid (D 1·2). In these solutions the action began at the point touched, and visibly spread over the surface; thus, when passive iron is immersed in electrolytes, the active state is able to spread rapidly from any active spot over the whole surface, whereas in distilled water activity spreads much more slowly. This was further shown by scratching the surface of passive iron. In nitric acid (D 1·2) and in copper sulphate solution action spreads rapidly from the scratch over the whole surface; in distilled water the rest of the surface remained passive for some time after the scratch had rusted.

Passivity was also destroyed by violently shaking the iron against the sides of the vessel or by touching with the fingers. Consequently, care must be exercised in washing and testing passive iron. Steel was found to behave in exactly the same way as wrought iron, except that it became active rather more readily.

Dilute Acids Destroy the Passivity of Iron.

(1) *Sulphuric Acid:*—Iron which had been rendered passive with 1 per cent. chromic acid was washed in distilled water, and immersed in dilute sulphuric acid of various strengths down to $N/10$. In all cases effervescence began in the course of some minutes, and on testing the iron with copper sulphate it was found to have become active.

(2) *Hydrochloric Acid:*—$N/10$-Acid rendered passive iron active in less than half a minute.

(3) *Acetic Acid:*—Passive iron was immersed in 5 per cent. acetic acid. It became active in fifteen minutes. In 2 per cent. acid the iron became active in twenty minutes, whilst in 1 per cent. acid the passivity was not destroyed for over an hour.

(4) *Formic Acid:*—A 1 per cent. solution rendered passive iron active in five minutes.

(5) *Citric Acid:*—A 1 per cent. solution destroyed passivity in twelve minutes.

(6) *Carbonic Acid:*—When passive iron was immersed in solutions of carbon dioxide it became active in times varying from half to one hour, depending on the extent of the passivity and on the strength of the solution of carbonic acid.

Reducing agents do not destroy passivity.

Passive iron was washed in distilled water, and immersed in solutions of formaldehyde, ammoniacal cuprous oxide, sodium hypophosphite, and alkaline dextrose. In all cases the iron remained passive.

Salt Solutions Destroy Passivity.

It has been known for some time that the presence of sodium chloride and other haloid salts prevents iron from attaining the passive state.

A sheet of passive iron was immersed in a 2 per cent. solution of sodium chloride. Rusting began in seven or eight minutes, which is also the time required for active iron to rust. Other sheets of passive iron were immersed in 2 per cent. sodium chloride for one minute and half a minute respectively. They were then tested with nitric acid (D 1·2), and found to be active. Solutions as dilute as 0·005 per cent. of sodium chloride gave similar results. Various other chlorides were employed, and all had the same vivifying effect. These were the chlorides of potassium, calcium, chromium, iron, and ammonium. Bromides and iodides were also found to destroy passivity. Other salts were then tried. Various nitrates and sulphates were found to destroy passivity, although not so rapidly as the haloid salts.

If any one of these salts is added to a solution which renders iron passive, the latter property should be nullified, and the iron remain active, and consequently rust. This was found to be actually the case. Sodium chloride was added to a solution of potassium chromate, and a piece of iron dropped in. Rusting readily occurred, although rather locally, and rapidly went deeply into the metal. The same result occurred when sodium chloride or one of the above-mentioned salts was added to a solution of sodium carbonate, potassium hydroxide, or hydrogen peroxide. Rusting occurred in every case. With chromic acid, the addition of sodium chloride caused a rapid action on iron, with reduction of the chromic acid and evolution of hydrogen. With potassium dichromate, which has a slightly acid reaction, the same result was obtained, except that there was less hydrogen produced.

The cause of the vivifying action of salts is elucidated by the results of the following experiments:

A sheet of iron was immersed in a solution of sodium chloride containing a few drops of phenolphthalein. A pink colour was rapidly developed on certain areas of the surface of the metal, indicating the formation of free alkali. It was found that the same effect was produced by other salts of the alkali metals, and was evidently caused by a difference of potential being set up, which resulted in slight electrolysis of the salt. In order to ascertain whether the difference of potential was set up by the oxidising action of the air on the iron, the experiment was repeated with complete exclusion of air. In this case no pink colour was formed.

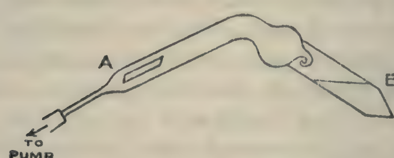
Air was then admitted, and as soon as it had diffused down to the iron, the pink colour appeared in patches as before, rusting occurring on the areas which were not coloured. It is obvious, therefore, that the difference of potential is due to the irregular action of the air on the iron, since it does not occur in absence of air.

These experiments were now repeated, using passive instead of active iron. Exactly the same phenomena were observed, showing that in the presence of sodium chloride the action of the air can also set up a difference of potential on passive iron.

As a consequence of these experiments it may be said that the vivifying effect of salts is due to an electrolytic effect. This is caused by a difference of potential set up on the surface of the iron by the action of the air, which causes the liberation of alkali from the salt at the cathodic portions, and of the acid radicle at the anodic portions. It is the latter which acts on the outer film of the iron, and destroys the passivity.

If this explanation is correct, salt solutions should not destroy the passivity of iron in absence of air, since no difference of potential

FIG. 1.



would then be set up. This was shown to be actually the case by the following experiment.

A bent glass tube *A B* was taken, and the end *B* drawn out to a fine capillary. A strip of dry passive iron (see below) was placed in the tube at the end *A*, which was then drawn out as shown. A 1 per cent. solution of sodium chloride was drawn in at *B*, and the capillary sealed. The end *A* was connected to a Sprengel pump, and the tube was completely evacuated, the solution being finally boiled to expel all air. The tube was then sealed at *A*, care being taken that no salt solution should touch the iron. The solution was now poured over on to the iron, allowed to remain there for half an hour, and then poured back again. The iron was washed free from sodium chloride by carefully distilling water over from *B* several times, keeping the limb *A* cool. Finally, the tube was opened, and the iron carefully transferred to a vessel containing copper sulphate solution, when it was found to be passive. Care was taken throughout not to shake the iron unduly. The experiment shows that in absence of air sodium chloride does

not destroy the passivity of iron. The strong vivifying effect is due to the combined action of both air and sodium chloride.

The Film Theory of Passivity.

The following experiments were made in order to gain further information respecting the production of a film as a probable cause of passivity:

Two polished sheets of iron, *A* and *B*, were taken. *A* was scratched with a sharp glass rod, and both were then immersed in a 1 per cent. solution of potassium dichromate overnight in separate vessels. On the following morning they were washed, and immersed in distilled water. The sheet *B* was then scratched. In eight to ten minutes the scratch on *B* began to show rusting, and after forty-five minutes was completely covered with rust, the rest of the surface remaining quite bright. The sheet *A* was entirely free from rust. This experiment shows that if the surface of iron is scratched after it has been rendered passive, active iron is exposed at the part scratched.

Similar results were obtained in other experiments. A sheet of iron was rendered passive in chromic acid. It was then washed in distilled water, and immersed in nitric acid (D 1·2). No action took place. The metal was now scratched with a sharp glass rod, when vigorous action at once set in at the scratch, and rapidly spread over the whole surface. On repeating the experiment in a copper sulphate solution, a similar result was obtained. Copper was at once deposited on the scratch, and the action rapidly spread outwards over the rest of the surface.

These experiments clearly indicate the presence of some kind of protective film on the surface of the passive iron. When a portion of this film is removed or disturbed, the original metal is thereby exposed, and the part so treated is rendered active. Violent shaking of the iron also may injure the film and cause activity.

That the film is not gaseous or in any way volatile was shown by the following experiments:

Several sheets of iron which had been rendered passive in chromic acid were obtained in the dry state, by washing first in distilled water and then in alcohol, and finally drying in a rapid current of air. The sheets so treated were found to retain their passivity for long periods in the dry state.

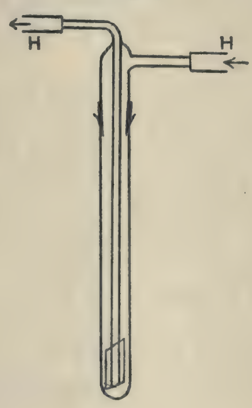
One of the sheets of dry passive iron was heated at 100° in a steam-oven for several hours, and was still passive. Another sheet was placed in a tube sealed at one end, which was then connected to a Sprengel pump and evacuated. It was heated at 100° for an

hour, when the iron was tested with copper sulphate solution, and found to be passive.

Higher temperatures were now employed, great care being taken to obtain a complete vacuum. Combustion tubing was used, and it was heated in a bath of soft solder (melting point 184°), the temperature being measured with a thermometer reading to 500°. In this way a sheet of passive iron was heated in a vacuum at 350° for fifteen minutes. After allowing to cool, the iron was tested with copper sulphate solution, when it was found to be passive. The experiment was repeated at higher and higher temperatures, and it was found that iron remained passive in a vacuum up to 400°. When the temperature was raised above 400° the passivity gradually disappeared.

Passive iron was heated in a sealed combustion tube, through which a current of hydrogen was passed, thus:

FIG. 2.



The hydrogen was dried, and passed over a heated copper spiral before entering the tube, so as to exclude all traces of oxygen. The tube was heated in a sulphuric acid bath at the lower temperatures, and in a solder-bath at the higher temperatures. The iron was tested at the end of each experiment with copper sulphate solution.

After heating at	200°	for 15 minutes,	the iron was	passive.
,,	220	,,	,,	,,
,,	240	,,	,,	,,
,,	250	,,	,,	active
,,	300	,,	,,	,,
,,	350	,,	,,	,,

Thus the passivity of iron was destroyed by heating in hydrogen between 240° and 250°.

Parallel experiments were done, in which passive iron was heated in nitrogen. They gave the same results as heating in a vacuum, namely, the passivity was not destroyed below 400°.

The temperature at which passivity was destroyed in hydrogen is evidently the same as the temperature at which the magnetic oxide begins to be reduced when heated in hydrogen.

This was further shown to be the case by the following experiment: A sheet of iron was coated with an extremely thin film of oxide by carefully heating in air or steam until it had assumed a slight orange colour. It was then heated in a current of hydrogen. Between 240° and 250° the oxide film was reduced, and disappeared.

These results afford strong evidence in favour of the probable existence of a film of oxide on the surface of passive iron.

The Passivity of Zinc.

In the case of zinc the passive state was shown by means of the same tests as those employed with iron.

(1) *Copper Sulphate Solution:*—Ordinary zinc, which is in the active state, is immediately attacked by a dilute solution of copper sulphate (0·5 per cent.), a dark layer of copper being at once deposited. In the passive state, however, zinc remains quite bright in copper sulphate solution for several minutes, and then a furry deposit of copper slowly begins to form.

(2) *Oxidation in Distilled Water:*—A bright sheet of active zinc begins to show oxidation in distilled water in fifteen minutes, and after one or two hours the oxidation has become general. Passive zinc, on the other hand, shows no oxidation in distilled water for many days, and often for several weeks.

Agents which Render Zinc Passive.

A solution of potassium dichromate was found to be the best agent for rendering zinc passive. Bright sheets of zinc were immersed in a 1 per cent. solution of potassium dichromate overnight. Being quite bright they were washed, and tested by the above methods. They were quite passive, both to copper sulphate solution and aerial oxidation in distilled water.

Solutions of chromic acid between 0·01 and 0·1 per cent. were also found to render zinc passive to both tests. A 1 per cent. solution, however, acted on the metal, with the formation of a layer of chromate. A 1 per cent. solution of potassium chromate rendered zinc passive towards copper sulphate solution, and towards oxidation in distilled water, although not so completely as did potassium

dichromate. Two per cent. solutions of sodium carbonate and of borax also rendered zinc partly passive. Stronger solutions had a direct action on the metal, which was also the case with potassium hydroxide and other strong alkalis.

Effect of Scratching the Surface of Passive Zinc.

A sheet of zinc which had been rendered passive in potassium dichromate was washed in distilled water, and scratched with a sharp glass rod. On immersing in copper sulphate solution, the scratch was immediately blackened by deposition of copper, the rest of the surface remaining bright for some time. When active zinc was treated in the same way, the scratch made no difference, the whole surface being immediately blackened. Another sheet of passive zinc was immersed in distilled water, and scratched as before. Oxidation rapidly began on the scratch, and after several days this was completely oxidised; the rest of the surface remained bright for a week or two.

These experiments afford strong evidence of a protective film on the surface of passive zinc, as was found in the case of iron.

The passivity of zinc is not destroyed by the action of dissolved air nearly so readily as that of iron. This is shown by its remaining unoxidised in distilled water for much longer periods. Also, salt solutions do not vivify passive zinc so readily as they do passive iron.

On the other hand, however, zinc largely loses its passivity on washing with alcohol, and drying. Consequently, some experiments in which dry passive zinc was heated in hydrogen were not found to be of much value in determining the nature of the protective film. Also, zinc oxide is not reduced by heating in hydrogen until after the melting point of the metal is reached.

The Passivity of Magnesium.

Magnesium will remain unoxidised for long periods if previously immersed in solutions of potassium dichromate or chromate. This is due to the fact that these reagents render it passive, as the following experiments show.

A sheet of magnesium was immersed for forty-eight hours in a 1 per cent. solution of potassium dichromate. It was then washed, and immersed in distilled water. A sheet of ordinary magnesium was also immersed in distilled water at the same time. The surface of the latter was almost immediately covered with bubbles of hydrogen, and in ten minutes visible oxidation had begun. The passive magnesium remained unchanged, and no gas was formed for

half an hour. The active magnesium then showed general oxidation over the whole surface. In two hours the passive sheet was quite bright, but showed slight effervescence. After twenty-four hours it was still bright; general oxidation had set in after forty-eight hours' immersion.

A similar experiment was performed, using a 1 per cent. solution of potassium chromate instead of dichromate. The passive magnesium only showed slight effervescence after half an hour, and remained bright for twenty-four hours, when general oxidation set in. The active metal began to oxidise in ten minutes as before.

Chromic acid has a direct action on magnesium, the surface of the metal becoming tarnished.

The Passivity of Copper.

Copper is rendered passive by immersion in solutions of chromic acid, potassium dichromate, and potassium chromate. Potassium hydroxide does not render copper passive, nor does it inhibit oxidation of the metal. The passive condition was shown by the following experiments:

(1) A sheet of pure copper was immersed in a 1 per cent. solution of potassium dichromate for about twelve hours. It was then washed, and immersed in distilled water. A similar sheet of active copper was also immersed in distilled water at the same time. The latter showed oxidation in the form of a thin film after three days. After a week the surface was much discoloured. The passive copper, on the other hand, had remained perfectly bright. After three weeks the surface of the active copper was completely oxidised, that of the passive copper being quite bright, and remaining so for over a month.

(2) Two sheets of copper, one of which had been immersed overnight in a 1 per cent. solution of potassium dichromate, were placed in separate vessels. A 0·1 per cent. solution of silver nitrate was poured over both. The active copper was at once acted on, being covered with a steely-blue film of silver. The passive copper remained unchanged for three or four minutes, and then a furry, grey deposit of silver slowly began to form.

(3) The previous experiment was repeated, using a dilute solution of mercurous nitrate instead of silver nitrate. Similar results were obtained.

(4) A dilute solution of silver acetate caused a deposit of silver on active copper in a few seconds. Passive copper was not acted on for more than half an hour.

Cause of the Passivity of Copper.

(1) Some passive copper was washed, and immersed in distilled water. It was then scratched with a sharp glass rod. In two days the scratch had begun to oxidise, and after a week was completely coloured dark red or black, the rest of the surface remaining perfectly bright. A piece of active copper was treated in the same way, but the scratch made practically no difference, and general oxidation began in the usual way in a few hours.

(2) A sheet of passive copper was scratched, and immersed in silver nitrate solution. The scratch was immediately blackened by deposition of silver, the rest of the surface remaining unchanged for some time. When active copper was treated in the same way, the whole surface was immediately blackened. The experiment was repeated with silver acetate with the same results.

(3) A sheet of copper was carefully polished with fine emery, and immersed overnight in a 5 per cent. solution of potassium dichromate. It was then washed, and carefully dried with a soft cloth. One-half of the surface was now polished up again with the same emery as before, care being taken throughout not to touch the metal with the fingers. On comparing the two portions, it was observed that the one not so recently polished was of a slightly redder colour than the other. The sheet was now immersed in distilled water in a covered gas-jar, and left to remain. In three days general oxidation had begun on the more recently polished portion, the rest of the surface being unchanged. After ten days the active portion had oxidised copiously, the rest of the surface remaining perfectly bright.

These experiments show that passive copper is covered with a protective film, and that the colour of the metal is rendered slightly redder in consequence.

In order to ascertain whether the film on passive copper is non-metallic, the rate at which passive copper amalgamates with mercury was compared with that of active copper. Two sheets of copper, one active and the other passive, were pressed down into mercury by means of glass rods hooked at the end, and the whole covered with distilled water. In fifteen minutes the active copper showed distinct amalgamation, whereas the passive copper did not begin to amalgamate for several hours, and even then only slowly. It is therefore improbable that the protective film consists of metal in an abnormal physical condition, and the evidence points to the conclusion that it is an oxide.

To show whether copper is oxidised by the action of chromates, a sheet of the metal was immersed in a solution of potassium chromate

to which ammonia had been added. A rapid action took place, copper passing into solution, and the chromate being reduced. Ammonia solution by itself has a much slower solvent action on copper, due to the oxidising action of the air. In both cases the oxide is dissolved by the ammonia as rapidly as it is formed. In this way the oxidising action of the chromate is rendered continuous by the constant exposure of a fresh surface of the metal.

The same result was obtained by the addition of dilute sulphuric or hydrochloric acid instead of ammonia. In this case the acid dissolves the film of oxide; thus, the copper passes into solution, and the chromate is reduced.

These results afford strong evidence that chromic acid and the chromates render copper passive by the production of a film of oxide on the surface of the metal.

Support for this view was also obtained by the action of the following solutions on passive copper:

Sulphuric Acid:—Passive copper was immersed in sulphuric acid of various dilutions down to $N/50$. In all cases the passivity was destroyed within two or three minutes.

Hydrochloric Acid:—Passive copper was treated with $N/50$-hydrochloric acid. On testing with silver acetate solution it was found to have become active.

Ferrous Sulphate:—On treating passive copper with a solution of ferrous sulphate, it was rendered active. A solution of ferrous sulphate dissolves copper oxide, with formation of ferric hydroxide.

Citric Acid.—A 10 per cent. solution rendered passive copper active.

These four reagents all dissolve copper oxide, and they all render passive copper active. Other acids which dissolve copper oxide also destroy the passivity of copper.

Copper rapidly loses its passivity when dried by washing in alcohol, and it is known that finely divided cuprous oxide is rapidly reduced by alcohol.

The Passivity of Lead.

Lead appears to behave similarly to copper and zinc, but the action in this case was not minutely studied.

Conclusions.

The results of this investigation leave little room for doubt that the observed passivity is due to the presence of a film of oxide on the surface of each metal. With iron this film remains intact on heating in a vacuum to temperatures as high as 400°. It cannot therefore be composed of a gas film. The film is, however, destroyed

by heating in hydrogen at 250°, the temperature at which magnetic iron oxide begins to be reduced. This is strong evidence in favour of the film being composed of an oxide of iron, and this explanation is supported by the fact that many dilute acids which dissolve the oxides of iron also destroy passivity. It is more difficult, however, to explain the action of the alkalis on this basis. It is known, however, that under certain conditions iron can be oxidised by alkalis with the production of a visible film of oxide. Presumably such oxidation can only take place with the liberation of hydrogen, and it has not so far been recognised that iron can react with cold dilute alkalis.

The strong vivifying effect of salt solutions, and especially of the haloid salts, is shown to be due to an electrolytic action, in which the acidic ion is liberated and attacks the film.

Zinc, copper, and magnesium can also assume the passive state. The passivity of zinc and copper is to be attributed to the formation of a protective film, which, in the case of copper, causes the metal to assume a slightly redder colour. The film is non-metallic, since it interferes with the amalgamation of copper by mercury.

The passivity of copper is destroyed by various reagents which dissolve the oxides of copper. Also, chromic acid and the chromates have been shown to exert an oxidising action on copper. It is therefore concluded that the passivity of copper is due to the formation of a film of oxide, probably cuprous oxide, on the surface of the metal. The cases of zinc, lead, and magnesium are no doubt also to be explained by the formation of films of the oxides of these metals.

Scientific Department,
Imperial Institute.

The Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society:

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
ROYAL COLLEGE OF SCIENCE,
SOUTH KENSINGTON,
LONDON, S.W.
October 4th, 1911.

GENTLEMEN,

I beg to forward you the Annual Report of the International Committee on Atomic Weights for 1912, to which I have appended, as desired by them, the signatures of Professors Clarke, Ostwald, and Urbain.

Slight changes have been made in the atomic weights of calcium, erbium, iron, mercury, tantalum, and vanadium, which are indicated, in accordance with a suggestion received from Germany, by asterisks.

The only addition to the list of elements is that of niton (radium emanation), with the symbol Nt, and the atomic weight 222·4, as determined by Gray and Ramsay. This is in fair agreement with the value calculated by Debierne from observations on the rate of flow of the gas.

I have the honour to be, Gentlemen,
Your obedient servant,
T. E. THORPE.

To the Hon. Secretaries,
The Chemical Society,
Burlington House,
London, W.

Report of the International Committee on Atomic Weights, 1912.

Since the report of the Committee for 1911 was prepared, a number of important determinations of atomic weight have been published, which may be summarised as follows:

Nitrogen.—Guye and Drouginine (*J. Chim. Phys.*, 1910, **8**, 473), from seven analyses of N_2O_4, find, in mean, $N = 14·010$.

Sulphur.—Burt and Usher (*Proc. Roy. Soc.*, 1911, *A*, **85**, 82), by analysis of nitrogen sulphide, N_4S_4, have determined the ratios $S:N::1·0:0·43687$. Hence, calculating with $N = 14·009$, $S = 32·067$, in good agreement with the accepted value.

Chlorine.—Burt and Gray (*Chem. News*, 1911, **103**, 161 and 170) have continued their work upon the density of hydrochloric acid, and confirmed their former determination of $Cl = 35·46$.

Iodine.—Baxter (*J. Amer. Chem., Soc.*, 1910, **32**, 1591) has re-determined the ratio of iodine to silver with extreme care. Combining his results with the previously-determined ratio of silver to iodine pentoxide, he finds Ag=107·864 and I=126·913. The value for silver varies from that found by Richards and Willard, and the discrepancy is as yet unexplained.

Sodium.—Goldbaum (*J. Amer. Chem. Soc.*, 1911, **33**, 35) has made analyses of sodium chloride and bromide by a new electrolytic method. The salts were electrolysed with a mercury anode and a weighed silver cathode, and on the latter the halogen was collected in weighable form. From the chloride, with Cl=35·458, Goldbaum found Na=22·997; the bromide, with Br=79·920, gave Na=22·998.

Calcium.—Two papers by Richards and Hönigschmid (*J. Amer. Chem. Soc.*, 1910, **32**, 1577; 1911, **33**, 28) on the atomic weight of calcium have appeared. From analyses of calcium bromide, Ca=40·070, when Ag=107·88. From analyses of the chloride, Ca=40·074. The value 40·07 is adopted in the table at the end of this report.

Cadmium.—Perdue and Hulett (*J. Physical Chem.*, 1911, **15**, 155; see also Richards, *J. Amer. Chem. Soc.*, 1911, **33**, 888), from electrolytic analyses of cadmium sulphate, conclude that the atomic weight of cadmium is near 112·30. This is lower than the accepted value, but as the investigation is being continued with other salts of cadmium, any change in the table should be deferred.

Mercury.—Easley (*J. Amer. Chem. Soc.*, 1910, **32**, 1117) has continued his work on the atomic weight of mercury, varying his methods. New analyses of the chloride give Hg=200·63, in confirmation of his former determinations. In a private communication he states that analyses of the bromide lead to the same value. The new figure, Hg=200·6, should be adopted.

Vanadium.—McAdam (*J. Amer. Chem. Soc.*, 1910, **32**, 1603), by reducing sodium vanadate to sodium chloride, by heating in a stream of dry hydrochloric acid, finds V=50·967, or 51 in round numbers. The latter figure is as probable as any.

Tantalum.—Balke (*J. Amer. Chem. Soc.*, 1910, **32**, 1127), by hydrolysis of tantalum pentachloride, has determined the ratio $2TaCl_5 : Ta_2O_5$. The mean of five concordant determinations gives Ta=181·52, when Cl=35·46. The rounded-off value 181·5 should be accepted.

Tellurium.—Flint (*Amer. J. Sci.*, 1910, [iv], **30**, 209) has continued the work reported by Browning and Flint in 1909 on the fractionation of tellurium by hydrolysis of the tetrachloride. With successive fractions the atomic weight steadily decreased. Seven analyses of the basic nitrate representing the tenth fractionation gave values for Te ranging from 124·25 to 124·42. As the work

is still in progress, any acceptance of these low figures would be premature.

Iron.—Baxter, Thorvaldson, and Cobb (*J. Amer. Chem. Soc.*, 1911, **33**, 319), from analyses of ferrous bromide, find Fe = 55·838 when Ag = 107·88. In another communication (*ibid.*, p. 337), Baxter and Thorvaldson find Fe = 55·836. The latter figure is the mean of two series, *meteoric* iron being taken as the starting point. The value 55·84 is given in the table.

Uranium.—Oechsner de Coninck (*Compt. rend.*, 1911, **152**, 711 and 1179), by reduction of UO_2Cl_2 and UO_3,H_2O to UO_2 in hydrogen, concludes that U = 238·5. The work is only approximate in character.

Scandium.—Meyer and Winter (*Zeitsch. anorg. Chem.*, 1910, **67**, 398), in a preliminary series of experiments, find values for Sc ranging from 44·86 to 45·37; in mean, 45·12. This is higher than the recognised value, but its adoption would be premature. More details are needed.

Neodymium.—By extended and careful analyses of the chloride, Baxter and Chapin (*Proc. Amer. Acad.*, **46**, 215) have redetermined the atomic weight of neodymium. From the ratio $NdCl_3:3Ag$, Nd = 144·268. From the ratio $NdCl_3:3AgCl$, Nd = 144·272. A small correction raises the value to 144·275. The rounded-off value 144·3, given in the table, may be properly retained.

Erbium.—Hofmann (*Ber.*, 1910, **43**, 2635), from analyses and syntheses of the sulphate of "neoerbium," finds Er = 167·68. This may be rounded to 167·7.

Argon.—Determinations of the density of argon, by Fischer and Froboese (*Ber.*, 1911, **44**, 92), give a mean value of 19·95. Hence A = 39·90.

Niton.—Gray and Ramsay (*Proc. Roy. Soc.*, 1910, *A*, **84**, 536), with the aid of the microbalance, have determined the density of the gaseous emanation from radium, to which they give the name *niton*. The mean value found gives Nt = 223, but the value 222·4 is preferred (compare also Debierne, *Compt. rend.*, 1910, **150**, 1740). The gas is a member of the argon group, and seems to be entitled to recognition in the table.

The table of atomic weights for 1912 follows. In accordance with a suggestion received from Germany, the changed values are indicated by an asterisk. The changes are few in number, and only in two cases are they large.

F. W. Clarke.
W. Ostwald.
T. E. Thorpe.
G. Urbain.

1912.

International Atomic Weights.

		O = 16.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·88
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium*	Ca	40·07
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium*	Er	167·7
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	3·99
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron*	Fe	55·84
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	6·94
Lutecium	Lu	174·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury*	Hg	200·6
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton* (radium emanation)	Nt	222·4
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·07
Tantalum*	Ta	181·5
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·4
Thulium	Tm	168·5
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium*	V	51·0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	172·0
Yttrium	Yt	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

CCX.—*The Active Constituents of the Indian Solanaceous Plants* Datura Stramonium, D. fastuosa, *and* D. Metel.

By Albert Edward Andrews.

Although the solanaceous plants *Datura Stramonium*, *D. fastuosa*, and *D. Metel* grown in Europe have been investigated by several workers, yet with the single exception of an article in the "Bulletin of the Imperial Institute" (1905, **2**, 224) giving the results of the examination of a specimen of *Datura Stramonium* seeds, no chemical investigation of these plants as grown in India appears to have been published, notwithstanding that their medicinal and poisonous properties have long been recognised in that country. For this reason, and with a view to their possible commercial utilisation, samples of these plants have from time to time been investigated in the Scientific and Technical Department of the Imperial Institute, and it is thought that it would be of interest to record the results obtained, especially as differences of climate and soil are known to produce considerable alteration in the constituents of plants. In carrying out this investigation, the chief aim has been to determine the amount and nature of the alkaloidal constituents, and compare them with those from the same species grown elsewhere.

The Indian species of *Datura* grow wild, and have long been known to the people of India for their intoxicating and narcotic properties. *D. Stramonium* is met with in the temperate Himalaya from Baluchistan and Kashmer to Sikkim. *D. fastuosa* is a small shrub found all over the tropical parts of India, and is said to be the most common and abundant species. *D. Metel* grows chiefly on the North-West Himalaya and the mountains of the Deccan.

The material used in the present investigation was kindly sent by the Officiating Reporter on Economic Products to the Government of India at the instance of Professor Wyndham R. Dunstan, under whose direction this work has been carried out.

Experimental.

Extraction and Estimation of the "Total Alkaloid."

The following was the general method employed in the examination of the various samples:

The finely ground material is exhausted by percolation with cold alcohol, and the solvent distilled off under diminished pressure until

practically the whole has been removed. The semi-solid extract is well agitated with small quantities of warm water, and then finally with very dilute sulphuric acid to ensure the complete separation of the alkaloid. The filtered aqueous acid liquid is shaken with ether, then made weakly alkaline with dilute ammonia, and shaken several times with chloroform to extract the alkaloid. Each portion of chloroform used to extract the alkaloid is in turn transferred to a second separator, washed with a little water, then dried over anhydrous sodium sulphate, and the total chloroform extract distilled under diminished pressure at a temperature not exceeding 40°. The total crude alkaloid thus obtained is then purified, and at the same time separated into two fractions. The residue of alkaloid is dissolved in a small excess of very dilute sulphuric acid, and the solution, filtered if necessary, is shaken with ether to remove traces of colouring matter and other impurities soluble in ether; the aqueous liquid is then made slightly alkaline with dilute ammonia, and extracted with three or four portions of ether and then with chloroform. Both the ether and chloroform solutions of the alkaloid are washed and freed from water as before noted, and the two fractions of alkaloid obtained by the distillation of the solvents are dried in a vacuous desiccator and weighed. The combined weights of the two extracts give the "total alkaloid" contained in the sample.

The separation of the total alkaloid into two fractions is done as a preliminary step in the identification of the constituent alkaloids, for should more than one alkaloid be present a partial separation is obtained, and the identification of the alkaloids facilitated.

The Identity of the Alkaloids.

In cases where hyoscyamine is the only alkaloid, or else largely predominates, the crystalline nature of the fraction extracted with chloroform indicates its presence; otherwise, the total alkaloid as weighed is amorphous. The aurichlorides are next prepared from each of the two fractions, and this salt is then fractionally crystallised until fractions of definite melting point are obtained. The alkaloids are then recovered from these fractions, and are further examined, following the clue to their identity given by the melting points of the gold salts.

In the case of scopolamine the identity was established by the melting points and general properties of the aurichloride, hydrobromide, and picrate, as compared with the same salts prepared and examined under identical conditions from a sample of Merck's scopolamine hydrobromide represented as agreeing with E. Schmidt's alkaloid, and also with the tests of the German Pharmacopœia.

There was complete agreement between the scopolamine isolated from the different plants and this sample of alkaloid.

The hyoscyamine isolated from the different plants in the course of this investigation was obtained in white, lustrous, hair-like crystals, melting at 106°, and having $[\alpha]_D$ $-20.75°$ at 21°. The following salts were prepared:

The aurichloride	melting at	159·5°.
The hydrobromide	,, ,,	149—150°.
The sulphate	,, ,,	209—210°.
The picrate	,, ,,	162—163°.

As will be seen from the tabulated results, there was no indication of atropine in any of the *Datura Stramonium* or *D. fastuosa* samples. In the case of *D. Metel*, however, there was evidence of

Results of examination of *Datura Stramonium* samples from the Punjab.

Part of plant.	Percentage of total alkaloid. In material as received.	Percentage of total alkaloid. Calculated on water-free material.	Alkaloids present.	Remarks.
Stems of small plant	0·23	0·25	Hyoscyamine and scopolamine	These alkaloids were present in the proportion of about 3 or 4 to 1 respectively
Stems of large plant	0·23	0·26	Hyoscyamine and scopolamine	There appeared to be rather less scopolamine present than in the previous samples
Leaves of small plant	0·42	0·45	Hyoscyamine only	There was no indication of the presence of any other alkaloid
Leaves of large plant	0·38	0·41	Hyoscyamine and scopolamine	These alkaloids were present in the proportion of about 4 to 1 respectively
Fruits of small plant	0·42	0·46	Hyoscyamine and scopolamine	These alkaloids were present in the proportion of about 4 to 1 respectively
Fruits of large plant	0·43	0·46	Hyoscyamine only	There was no indication of the presence of any other alkaloid
Roots* of both large and small plants	0·19	0·21	Hyoscyamine and scopolamine and another alkaloid not identified	The hyoscyamine and scopolamine were present in about equal quantities
Very small complete plant	0·20	0·22	Scopolamine only	There was no indication of the presence of any alkaloid other than scopolamine

* The large quantity of potassium chloride and nitrate present in this sample was particularly noticeable. The alcoholic percolate was found to contain an amount of these salts which, calculated as K_2O, equalled 1·42 per cent. of the roots.

Results of examination of *Datura Stramonium* samples from Madras.

Part of Plant.	Percentage of total alkaloid. In material as received.	Calculated on water-free material.	Alkaloids present.	Remarks.
Leaves	0·38	0·42	Hyoscyamine and scopolamine	These alkaloids were present in the proportion of about 5 to 1 respectively
Seeds	0·173	0·186	Hyoscyamine and scopolamine	These alkaloids were present in the proportion of about 3 to 1 respectively. There was in addition a small quantity of impure alkaloid, probably hyoscyamine

the presence of a small proportion of atropine, but the amount was insufficient fully to establish its identity. In these cases the aurichloride was obtained in non-lustrous crystals, melting at 135—140°, and the alkaloid recovered from these was optically inactive.

The tabulated statements give the results obtained with the different parts of the Indian solanaceous plants, *Datura Stramonium*, *D. fastuosa*, and *D. Metel*, and show (1) the amount of total alkaloid contained in the particular part of the plant, (2) the constituent alkaloids which have been identified, and (3) the approximate proportions of the different alkaloids in those cases where more than a single alkaloid is present.

The following points may be noted from the tabulated results for the *Datura Stramonium* samples:

In the samples from the Punjab the percentage of total alkaloid in similar parts of the large and small plants was practically the same, whether in the fruits, stems, or leaves.

The alkaloids in all of the samples were either hyoscyamine or scopolamine, or both in varying proportions. Only in the case of the roots was there evidence of a third alkaloid. There was no indication of atropine in any of the samples.

Hyoscyamine was the only alkaloid found in the leaves of the small plant and in the fruits of the large plant. In each case it was present to the extent of nearly 0·5 per cent., and could readily be isolated in a crystalline condition.

Scopolamine was the only alkaloid in the very small plant. With this one exception, hyoscyamine was the predominant alkaloid. The proportion of hyoscyamine and scopolamine in the stems of the large and small plants shows very little variation, but in the

case of the fruits and the leaves it is noticeable that scopolamine is absent in the leaves of the small plant and in the fruits of the large plant. The following table showing the distribution of the alkaloids in the different parts of the small and large plants indicates these points more clearly. It should be mentioned that these plants were collected at one time in the same district of the Punjab.

	Stems.	Leaves.	Fruits.	Whole plant.	
Very small plant	—	—	—	Scopolamine	
Small plant	3 or 4 parts of hyoscyamine to 1 part of scopolamine	Hyoscyamine only	4 parts of hyoscyamine to 1 part of scopolamine	—	Hyoscyamine and scopolamine in about equal proportions, and a small proportion of a third alkaloid not identified
Large plant	Hyoscyamine and scopolamine. Rather less of the latter alkaloid than in stems of small plant	4 parts of hyoscyamine to 1 part of scopolamine	Hyoscyamine only	—	

In the following table the percentages of total alkaloid found in the Indian specimens of *Datura Stramonium* are compared with the recorded figures for similar parts of the plant grown elsewhere:

Part of plant.	Indian specimens.	Specimens from other countries.		
Seeds	0·186	0·21 to 0·48 (European)		
	0·46*	0·35 (Egyptian)		
Leaves	0·41 to 0·45	Up to 0·4 (European)		
Stems	0·25 to 0·26	Main stems	0·09	(European)
		Upper branches	0·36	
		Average	0·22	
Roots	0·214	Main roots	0·10	(European)
		Rootlets	0·25	
		Average	0·17	

* This was the percentage in two samples of the fruits, that is, seeds and capsules together; the alkaloid is chiefly present in the seeds, consequently the figure for the fruits is lower than it would be for the seeds alone.

These figures clearly indicate that Indian *Datura Stramonium* bears favourable comparison with the European and Egyptian plants as regards the amount of total alkaloid that it contains. In the plants from the latter sources, hyoscyamine is generally stated to be the only or the main alkaloid present, being in some cases associated with a small proportion of atropine. The presence of scopolamine in some of the Indian samples appears, therefore, to be a point of difference.

Results of examination of *Datura fastuosa* var. black, from Assam.

Part of plant.	Percentage of total alkaloid in material as received.	Alkaloids present.	Remarks.
Twigs and leaves	0·119	Scopolamine and hyoscyamine	These alkaloids were present in the proportion of about 4 to 1 respectively. There was in addition a small proportion of amorphous alkaloid
Roots	0·101	Scopolamine only	There was no indication of either hyoscyamine or atropine. A small proportion of amorphous alkaloid was present
Fruits	0·202	Scopolamine only	There was no indication of either hyoscyamine or atropine. A small proportion of amorphous alkaloid was present

It is noticeable in the above results for *D. fastuosa* that scopolamine is the only alkaloid in the roots and fruits, and is the predominant alkaloid in the twigs and leaves of the plant. The seeds of this species grown in Europe contain about the same amount of alkaloid as that found for the Indian plant, and contain scopolamine as the main alkaloid associated with a small proportion of hyoscyamine and a little atropine.

Results of examination of *Datura Metel* samples from the Punjab.

Part of plant.	Percentage of total alkaloid.		Alkaloids.	Remarks.
	In material as received.	Calculated on water-free material.		
Leaves from Lyallpur	0·22	0·25	Scopolamine	A small proportion of another alkaloid, apparently atropine, was present
Seeds from Lyallpur	0·21	0·23	Scopolamine	Ditto
Seeds from Patiala	0·23	0·25	Hyoscyamine and scopolamine	These alkaloids were present in the proportion of about 2 to 1 respectively. A small proportion of another alkaloid was present, which appeared to be atropine
Capsules from Patiala	0·10	0·12	Scopolamine only	No indication of the presence of any other alkaloid

E. Schmidt (*Arch. Pharm.*, 1905, **243**, 309; 1910, **248**, 641) examined *D. Metel* cultivated in France, and found that scopolamine is present in all parts of the plant and is unaccompanied by any notable quantity of other mydriatic bases. The dried leaves

contain 0·55 per cent., and the seeds 0·5 per cent., of scopolamine. Kircher (*Arch. Pharm.*, 1905, **243**, 309) confirmed Schmidt's figures, and drew the conclusion that scopolamine formed the bulk of the alkaloid, being accompanied by only small proportions of hyoscyamine and atropine.

On comparing these results with those in the table, it appears that in the Indian plant the percentage of total alkaloid in the seeds and in the leaves is only about one-half what it is in the European plant. The *D. Metel* seeds from Patiala appear to be exceptional in containing hyoscyamine as the predominant alkaloid, but the other three samples resemble the European plant in so far that scopolamine is almost unaccompanied by other mydriatic alkaloids.

SCIENTIFIC and TECHNICAL DEPARTMENT,
IMPERIAL INSTITUTE, S.W.

CCXI.—*A New Stereoisomeride of Cyanodihydrocarvone.*

By ARTHUR LAPWORTH and VICTOR STEELE.

IT has been shown that *d*-carvone unites with hydrogen cyanide in the presence of potassium cyanide at the ordinary temperature, yielding, in the first instance, a cyanodihydrocarvone:

$$CH_3\cdot \underset{(2)}{CH}<\begin{matrix}CO\text{———}CH_2\\ \underset{(3)}{CH}(CN)\cdot CH_2\end{matrix}>\underset{(1)}{CH}\cdot C\begin{matrix}\diagup CH_3\\ \diagdown CH_2\end{matrix}.$$

This substance contains three asymmetric carbon atoms, labelled 1, 2, and 3, whilst the original carvone contains the first only (Trans., 1906, **89**, 945 *et seq.*, and 1819 *et seq.*). *d*-Carvone may theoretically give rise to four stereoisomeric cyanodihydrocarvones, and evidence of the existence of at least two was obtained on a former occasion by showing that the one which had then been isolated in a pure form exhibited mutarotation in the presence of a trace of sodium ethoxide. It has since been observed that if the addition of the hydrogen cyanide takes place in hot solutions, a crystalline cyanodihydrocarvone is formed in considerable quantity, which has a rotatory power in the opposite sense to that of the isomeride previously described, and cannot be converted into the latter by traces of alkali. It is probable that it represents the third possible isomeride, and it appears to be partly converted into the fourth isomeride by small quantities of alkali in alcoholic

solution, as it then exhibits a small but definite mutarotation; the final value of the rotatory power attained is, however, about $[\alpha]_D$ −39·00° instead of $[\alpha]_D$ +15·4°, the value shown by the cyano-compound first discovered.

It would thus appear that the four isomerides may be divided into two pairs, the two members of each pair being dynamic isomerides at the ordinary temperature. At higher temperatures, in the presence of alkalis, all four are probably dynamic isomerides, as in this case hydrogen cyanide may be alternately eliminated and reabsorbed with considerable rapidity. It is known that the sign of an asymmetric carbon atom in the complex $^{a}_{b}{>}CH{\cdot}CO{\cdot}C⫶$ may undergo inversion, causing the effect of mutarotation in the presence of traces of alkalis. As the hydrogen atom in the group $>CH{\cdot}CN$ appears usually to be less labile than that in the group $>CH{\cdot}CO{\cdot}C⫶$, it appears highly probable that the mutarotations observed with the two crystalline cyanodihydrocarvones at the ordinary temperature may be attributed to the presence of the latter complex. If this is so, then the new cyano-compound and its dynamic isomeride differ from those obtained by the synthetic process at the ordinary temperature, by a change in the sign of the asymmetric carbon atom to which the cyano-group is attached. It was proved that the asymmetric carbon atom of the carvone complex itself had been unaffected, as both the crystalline cyano-compounds yielded pure *d*-carvone when boiled with solutions of alkali containing suspended ferrous hydroxide.

The new nitrile yields a new *amide* when hydrolysed by cold hydrogen chloride, but the carboxylic acids which are formed on further hydrolysis are identical with those previously obtained.

Experimental.

neo-*Cyanodihydrocarvone*, $C_{11}H_{15}ON$.

This substance was accidentally obtained, in the first instance, as the result of using a hot, instead of a cold, solution of potassium cyanide during the preparation of α-cyanodihydrocarvone by the process otherwise as previously described (Trans., 1906, **89**, 950), the yield being very small. It was found later that the following process gave yields of about 85 per cent. of the theoretical.

Thirty grams of potassium cyanide (100 per cent.), 80 c.c. of water, and 80 c.c. of spirit are together heated to boiling on the water-bath, and a boiling mixture of 60 grams of carvone and 30 c.c. of ethyl acetate is then added, heating being continued until complete solution takes place, an operation which usually occupies

about twelve to fifteen minutes. The whole is cooled and diluted with water, when the greater part of the nitrile separates in a solid form, and is removed by filtration, the filtrate being extracted with ether. The ethereal extract is washed with water, the solvent removed, and the residue added to the precipitated nitrile. The compound is purified by repeated crystallisation from alcohol:

0·2018 gave 0·5500 CO_2 and 0·1549 H_2O. C = 74·3; H = 8·3.
$C_{11}H_{15}ON$ requires C = 74·6; H = 8·5 per cent.

Experiments were made with the object of ascertaining whether the β-cyanodihydrocarvone could be obtained from the α-nitrile by the action of small quantities of alkalis or sodium ethoxide, but although change certainly occurs, the oils which are formed do not readily yield anything of a definite character. β-Cyanodihydrocarvone resembles its isomeride in regard to its behaviour towards the usual solvents, and crystallises from alcohol or benzene in needles, melting at 84°.

0·3618, made up to 25 c.c. with absolute alcohol, gave, in a 2-dcm. tube, $\alpha - 1·22°$, whence $[\alpha]_D$ $-42·1°$. After the addition of a trace of sodium ethoxide, the observed rotation was $-1·13°$, whence $[\alpha]_D^{11}$ $-39·00°$. That this slight fall was in the main due, as is the case of its isomeride, to isodynamic change seems probable, as the solution on spontaneous evaporation yielded a viscid liquid which crystallised only after some time; the solid then obtained was, however, identical with the original substance (compare Trans., 1906, **89**, 951).

The nitrile distils under the ordinary pressure without undergoing any appreciable isomeric change, but with slight charring. It behaves towards potassium permanganate and bromine as an unsaturated compound, exhibits distinct basic properties, dissolving appreciably in concentrated hydrochloric acid, and is not precipitated from the solution on addition of water. Although it is not quickly decomposed by a hot 5 per cent. solution of potassium hydroxide in alcohol, it rapidly loses hydrogen cyanide when boiled with concentrated alcoholic potassium hydroxide, carvone being liberated, and the change is more rapid and complete if ferrous hydroxide is also present to unite with the potassium cyanide as it is formed. In one experiment this nitrile was heated with a concentrated methyl-alcoholic solution of potassium hydroxide containing suspended ferrous hydroxide, for about fifteen minutes, the liquid being then diluted with water and distilled in a current of steam. The distillate was extracted with ether, the ethereal solution washed with a little water, dried, and freed from solvent. On distillation of the residue, the fraction boiling at 225° was collected;

this had the odour of ordinary carvone, and had the same rotatory power.

0·335, made up to 25 c.c. with absolute alcohol, gave, in a 2-dcm. tube, $\alpha + 1·68°$, whence $[\alpha]_D^{12} + 62·7°$, whilst carvone has $[\alpha]_D + 62°$ to $62·5°$ in this solvent.

The action of amyl nitrite and sodium ethoxide on the new nitrile was investigated.

Twelve grams of the pure nitrile were added to an ice-cold solution of 1·6 grams of sodium dissolved in 40 c.c. of absolute alcohol; 10 grams of amyl nitrite were then added slowly, the temperature being kept at 0°. After twelve hours, water (500 c.c.) was added, and the solution filtered from a little tarry matter. The filtrate was saturated with carbon dioxide, when a white, voluminous solid separated. This was collected, and after crystallisation from alcohol weighed 11 grams. It crystallised in slender needles, melting at 138—139°, and was identical with the active lactam obtained by Lapworth and Wechsler (Trans., 1907, **91**, 981) by a similar treatment of ordinary cyanodihydrocarvone; thus its melting point was not affected by admixture with that compound, and its rotatory power had the same value.

0·2055, made up to 25 c.c. with absolute alcohol, gave, in a 2-dcm. tube, $\alpha + 1·99°$, whence $[\alpha]_D^{14} + 121·04°$.

The compound described by Lapworth and Wechsler had $[\alpha]_D + 121°$ in alcohol.

The *phenylhydrazone*, $CN{\cdot}C_{10}H_{15}{:}N{\cdot}NHPh$, was prepared by warming together equimolecular proportions of the nitrile and phenylhydrazine for half an hour. It was purified by crystallisation from alcohol:

0·1836 gave 0·5075 CO_2 and 0·1305 H_2O. C = 75·4; H = 7·9.

$C_{17}H_{21}N_3$ requires C = 75·4; H = 7·9 per cent.

It closely resembles the isomeric hydrazone previously described (*loc. cit.*, p. 952), but separates from alcohol in slender needles, and is somewhat unstable, changing spontaneously into a dark red syrup. It melts and decomposes between 113° and 116°, according to the rate of heating.

The *oxime*, $CN{\cdot}C_{10}H_{15}{:}NOH$, crystallises from alcohol in flat needles, which melt at 182° with slight darkening. In other respects, it has much the same properties as the oxime of the α-cyanodihydrocarvone:

0·1993 gave 0·5007 CO_2 and 0·1512 H_2O. C = 68·5; H = 8·4.

$C_{11}H_{16}ON_2$ requires C = 68·7; H = 8·3 per cent.

Formation of Carboxylic Acids from β-Cyanodihydrocarvone.

Five grams of nitrile were left in contact with 40 grams of saturated aqueous hydrogen chloride for five days, the hydrolysis being completed by heating for two hours on the water-bath. The acid products of hydrolysis were finally obtained as a crystalline mass, which was rapidly washed with carbon disulphide. A colourless mass was left, which was crystallised from ethyl acetate:

0·1620 gave 0·3997 CO_2 and 0·1190 H_2O. C = 67·3; H = 8·2.

$C_{10}H_{15}O \cdot CO_2H$ requires C = 67·4; H = 8·2 per cent.

0·1463 required 7·5 c.c. $N/10$-NaOH for neutralisation, using phenolphthalein as indicator, hence equivalent = 195. The number calculated for a monobasic acid, $C_{11}H_{16}O_3$, is 196.

The product, as in the case of the hydrolysis of α-cyanodihydrocarvone, was found to be a mixture, the melting point being indefinite between 85° and 110°. As the whole did not melt below 100°, the mixture was placed on porous porcelain, and allowed to remain in the steam-oven for four hours. A small quantity of material was left, which appeared to be homogeneous, and after one or two crystallisations melted sharply at 135°. The quantity obtained in a pure state, however, was too small for further investigation.

On another occasion the crude product of hydrolysis was extracted repeatedly with boiling water, a treatment which left a dark-coloured, insoluble gum behind. On cooling the extract, the acids crystallised as a mixture of pure white needles and flat plates. By crystallisation from carbon tetrachloride, two fractions were obtained, the first being only sparingly soluble, and the other fairly readily so in that solvent. The first fraction was recrystallised, and separated in plates, melting sharply at 142—143°; it was proved to be identical with the β-acid obtained from ordinary cyanodihydrocarvone by the "mixed melting-point" method. The other fraction was crystallised twice from ethyl formate, and then melted sharply at 97°; it was proved to be identical with the α-acid obtained from ordinary cyanodihydrocarvone.

β-Cyanodihydrocarvonecarboxylamide, $NH_2 \cdot CO \cdot C_{10}H_{15}O$. — The nitrile (5 grams) was allowed to remain with saturated hydrobromic acid (10 c.c.) until it had dissolved, and a drop of the resulting liquid gave no precipitate on addition to water, when, on diluting with water and neutralising with sodium carbonate, the amide slowly separated in crystalline form. It was purified by crystallisation from alcohol:

0·2187 gave 0·5452 CO_2 and 0·1699 H_2O. C = 67·9; H = 8·6.

$C_{11}H_{17}O_2N$ requires C = 67·7; H = 8·7 per cent.

The amide, which closely resembles its isomeride in solubility in organic media, separates from ethyl acetate in flat needles, which, when heated, darken slightly at 200°, and melt at 218°. When it was mixed with the amide obtained from the α-nitrile, melting occurred at 180°, so that the compounds are not identical.

When the new amide is almost fully hydrolysed by means of hot alcoholic potassium hydroxide, the acidic product is a mixture of α- and β-dihydrocarvonecarboxylic acids. If, however, the heating occupies only a few minutes, and the resulting liquid is poured into water and acidified, a crystalline precipitate of an acid is obtained, which, after one crystallisation from water, melts at 141—142°, being practically pure α-dihydrocarvonecarboxylic acid, as was shown by the "mixed melting-point" method. It has previously been shown (Trans., 1906, **89**, 958) that the amide obtained from ordinary cyanodihydrocarvone, if hydrolysed by boiling with alcoholic potassium hydroxide, is converted into a dihydrocarvonecarboxylic acid. These experiments have since been repeated, the whole being heated for a short time only; the product, after one crystallisation from water, melted sharply at 97°, and was identical with the β-carboxylic acid, whilst the nearly pure α-acid was obtained on a former occasion by one of us.

The observations as to the conditions which lead to the production of either or both carboxylic acids from the isomeric amides are thus somewhat contradictory, so that the relationship between the compounds remains an open question.

SCHUNCK LABORATORY,
UNIVERSITY OF MANCHESTER.

CHEMICAL LABORATORY,
GOLDSMITHS' COLLEGE, NEW CROSS, S.E.

CCXII.—*Some Properties of Phenyl* iso*Propyl Ketone.*

By ARTHUR LAPWORTH and VICTOR STEELE.

IT is well known that ketones which contain the group $\cdot CO \cdot CH_2 \cdot$ condense readily with certain carboxylic esters in presence of sodium or sodium ethoxide, yielding β-diketones and alcohol, whilst ketones which contain only the complex $\cdot CO \cdot \dot{C}H$ do not take part in such a condensation. The theory of the mechanism of the reaction has been discussed on numerous occasions, and reference may be made to a paper by Clarke, Lapworth, and Wechsler (Trans., 1908, **93**, 30) for an historical summary.

With the view of obtaining some further evidence on the subject, the behaviour of phenyl *iso*propyl ketone towards such reagents has been investigated, as it was thought possible that this ketone might react with certain carboxylic acids in accordance with the following scheme (compare 1 (*b*), *loc. cit.*, p. 34):

$$\mathrm{R{\cdot}CO{\cdot}OEt + CHMe_2{\cdot}COPh} \longleftrightarrow \mathrm{R{\cdot}CO{\cdot}CMe_2{\cdot}COPh + HOEt}$$
$$\longleftrightarrow \mathrm{R{\cdot}CO{\cdot}CHMe_2 + OEt{\cdot}COPh}$$

yielding ethyl benzoate and a new ketone.

The ketone used in the first experiment was prepared from *iso*butyryl chloride and benzene by the Friedel-Crafts' reaction, and the acid chloride itself from a sample of calcium *iso*butyrate. When this ketone, after careful fractionation, was brought into contact with sodium and ethyl acetate, formate, benzoate, or oxalate, in ethereal solution, highly coloured liquids were produced, which, when shaken with water, yielded yellow aqueous extracts, from which acids precipitated small quantities of acidic oils. The latter gave violet or deep-brown colorations with ferric chloride, and, in general, deported themselves as β-diketones or β-ketonic esters.

Later the ketone was allowed to react with ethyl phthalate and sodium, as the ketonic compound, which would arise as the result of the above series of reactions, would then have had the structure (I), from which an acid could be obtained and easily identified,

$$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CO{\cdot}CHMe_2}\\ \mathrm{CO_2Et}\end{matrix} \qquad\qquad \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{C(:CMe_2)}\\ \mathrm{C(:NOH)}\end{matrix}{>}\mathrm{O}$$

(I.) (II.)

even if formed in comparatively small quantities, by means of its characteristic oxime-anhydride (II).

A red solution was formed in the cold, and to this alcoholic potassium hydroxide was added, and the whole heated for several hours on the water-bath, the ether being allowed to escape; hydroxylamine hydrochloride was then added, when, on cooling, a small quantity of a compound separated, which was at first thought to be the expected oxime-anhydride. It was collected, crystallised from alcohol, and analysed:

0·1996 gave 0·5009 CO_2 and 0·0921 H_2O. C = 68·3; H = 5·2.

$C_{10}H_9O_2N$ requires C = 68·0; H = 5·1 per cent.

It thus had the composition of *ethylidenephthalideoxime*,

$$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{C(:CHMe)}\\ \mathrm{C(:NOH)}\end{matrix}{>}\mathrm{O},$$

and melted at 111°; its identity with that compound was established by preparing a sample of the latter from synthetical ethylidenephthalide and hydroxylamine; the compounds were identical in all respects, and mixtures melted at the same temperature as either separately.

The formation of this substance in the above reaction suggested that the original ketone contained phenyl ethyl ketone, owing to the unsuspected presence of propionate in the sample of calcium *iso*butyrate. Repeated fractionation of the ketone did not serve appreciably to diminish its reactivity towards esters and sodium, and the whole was therefore converted into oxime, the latter carefully purified, and reconverted into ketone by the processes described below. When purified in this way, the ketone displayed complete indifference towards carboxylic esters (including ethyl phthalate) in presence of sodium even at the temperature of the water-bath; that is to say, no trace of ketonic compound other than the original one could be detected.

It must be concluded, therefore, either that phenyl *iso*propyl ketone does not react at all with carboxylic esters in the presence of sodium or sodium ethoxide, or that the product decomposes exclusively into its original generators. It would be interesting to ascertain whether di*iso*propyl ketone would react with ethyl phthalate and sodium yielding *iso*propylidenephthalide and ethyl *iso*butyrate, but this the authors have not had the opportunity to test.

Preparation of Ketoximes and their Use in the Purification of Ketones.

Phenyl iso*Propyl Ketoxime.*

Some five years ago the authors devised the following process for preparing oximes, and using these for the purification of ketones; as the methods have proved to be of very general applicability, the more important details may be given here.

In preparing oximes the main practical advance consisted in avoiding the use of water other than that possibly contained in the solvent alcohol; the quantity of solvent then necessary is, as a rule, greatly diminished, whilst the use of sodium acetate precludes the possibility of any appreciable hydrolysis or transformation of the oxime formed.

The ketone is dissolved in at least three times its weight of spirit of 94—100 per cent. strength, the quantity and percentage of solvent depending mainly on the solubility of the ketone in the boiling solvent. To the hot solution is added 1 to 1½ molecular proportions of solid hydroxylamine hydrochloride, and then at once excess of anhydrous sodium acetate; sodium chloride separates, but the whole is heated (at a temperature somewhat below that likely to cause bumping) until a drop of the solution, added to about ½ c.c. of 10 per cent. sodium hydroxide, gives a clear solution

with no odour of ketone. The whole is cooled, evaporated, if necessary, in cases where the ketone is sparingly soluble, and the bulk of solvent therefore considerable, mixed with water, and the oxime removed by filtration or by extraction with light petroleum or ether. Nearly quantitative yields have been obtained with most simple ketones experimented with, and such compounds as camphor-oxime are prepared much more easily and economically by this process than by those usually recommended. Crossley and Renouf found that a modification of this method gave good results with dimethyldihydroresorcin (compare Trans., 1909, **95**, 930, *footnote*), and it might with great advantage replace the older methods in nearly all cases.

The regeneration of the ketone from the pure oxime is accomplished most satisfactorily as follows. The oxime is heated for several hours on the water-bath with 3 to 4 parts by weight of 15 per cent. hydrochloric acid, and $\frac{1}{2}$ to $\frac{3}{4}$ part by weight of commercial formaldehyde (40 per cent.); the whole is cooled, poured into twice its bulk of water, extracted with ether, and the latter washed repeatedly with water, dried, and evaporated, and the residue purified by fractional distillation. The yields are from 85 to 95 per cent. of those theoretically possible in all cases tried, with the exception of oximes, such as that of camphor, which are very prone to undergo the Beckmann transformation.

Phenyl *iso*propyl ketone, purified in this manner, boiled at 217°, and had D^{15}_{15} 0·9886 (two specimens). (Found, C=81·1; H=8·2. Calc., C=81·1; H=8·1 per cent.)

The *semicarbazone* crystallised from alcohol in needles, melting at 181°:

0·1985 gave 0·4711 CO_2 and 0·1310 H_2O. C=64·7; H=7·3.

$C_{11}H_{15}ON_3$ requires C=64·4; H=7·3 per cent.

The oxime, purified by repeated crystallisation from light petroleum, crystallises from that solvent in transparent, lustrous, massive tablets, melting sharply at 94°. (Found, C=73·6; H=8·1. Calc., C=73·6; H=8·0 per cent.)

Rattner (*Ber.*, 1887, **20**, 206) describes the oxime as forming leaflets, melting at 58°, and Claus (*J. pr. Chem.*, 1892, [ii], **46**, 480) gives 61°.

The present authors, suspecting the possibility of stereoisomerism, have prepared the oxime in neutral solutions, in alkaline solutions of various strengths, and at temperatures varying from 15° to 100°, but in all cases the only form obtained was that melting at 94°. The oxime was only obtained in small plates or leaflets when the original ketone was contaminated with phenyl ethyl ketone, and

possibly a similar cause contributed to the results of Rattner and of Claus.

Phenyl ethyl ketoxime was prepared, for comparison with the above oxime, from phenyl ethyl ketone obtained by the interaction of magnesium ethyl bromide and benzonitrile. It had all the properties assigned to it by Pampel and Schmidt (*Ber.*, 1886, **19**, 2896).

Action of Ethyl Nitrite on Phenyl iso*Propyl Ketone in Presence of Sodium Ethoxide.*

It has been shown that certain ketones which contain the complex $\cdot CH_2\cdot CO\cdot CH<$ as part of a ring, although reacting at the $\cdot CH_2\cdot$ group when subjected to treatment with carboxylic esters in the presence of sodium ethoxide, are attacked by alkyl nitrites in similar circumstances at the $\cdot CH<$ group, ring scission taking place simultaneously probably in accordance with the following scheme (compare Clarke, Lapworth, and Wechsler, Trans., 1908, **93**, 35):

$$(1)\ R\cdot CO\cdot CHR'R'' + NO\cdot OEt = R\cdot CO\cdot C(NO)R'R'' + HOEt + NaOEt$$

$$(2)\ R\cdot CO\cdot C(NO)R'R'' + \begin{cases} 2NaOH \text{ or} \\ NaOEt \end{cases} = NaO\cdot N\!:\!CR'R'' + \begin{cases} R\cdot CO\cdot ONa \\ R\cdot CO\cdot OEt \end{cases} + H_2O.$$

No direct proof of the formation of ester was advanced at the time, and the reaction was not applied to any simple ketone. The following experiment confirming the above scheme was carried out by the present authors with highly purified phenyl *iso*propyl ketone.

Sodium (1·5 grams) was dissolved in about 25 c.c. of 99·5 per cent. alcohol, phenyl *iso*propyl ketone (10 grams) was then added, the whole being subsequently kept cold by means of ice-water while ethyl nitrite (5 grams) in strong spirit was slowly introduced. A white solid separated almost at once, and, at the end of two hours, was collected and identified as sodium benzoate (doubtless formed as above by the action of sodium hydroxide on the nitroxylated ketone forming the intermediate product of the reaction). The alcoholic mother liquor was diluted with water, the oil which separated being removed, washed, and dried; 2 grams of pure ethyl benzoate, boiling at 212°, were obtained by fractionation of this oil.

The alkaline mother liquor was acidified and extracted with ether, which was then washed with water, dried, and evaporated; the residue was a mixture which was fractionated by means of

light petroleum. From the more soluble portion acetoxime was readily separated and identified.

Some of the cost of this investigation was defrayed from a grant from the Government Grant Fund of the Royal Society, for which the authors desire to acknowledge their indebtedness.

SCHUNCK LABORATORY, UNIVERSITY OF MANCHESTER.

CHEMISTRY DEPARTMENT, GOLDSMITHS' COLLEGE, NEW CROSS, S.E.

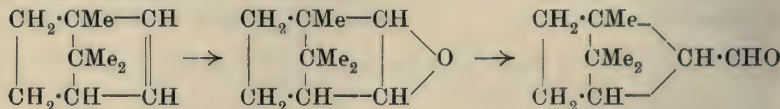
CCXIII.—*Contributions to the Chemistry of the Terpenes. Part X. The Action of Chromyl Chloride, Nitrous Acid, and Nitric Acid on Bornylene.*

By GEORGE GERALD HENDERSON and ISIDOR MORRIS HEILBRON.

UP to the present time few of the derivatives of bornylene have been prepared, although the interesting relationship of this terpene to camphene, borneol, and camphor renders the full investigation of its chemical character desirable. We have accordingly begun to study these compounds, and the present paper contains an account of the results obtained by oxidising bornylene with chromyl chloride, and by attacking it with nitrous and nitric acids respectively.

Bredt and Jagelki (*Annalen*, 1900, **310**, 112) observed that camphene, on treatment with chromyl chloride, yields an additive product which reacts with water, giving as sole product camphenilanaldehyde, $C_9H_{15}\cdot CHO$. Camphenilanic acid, $C_9H_{15}\cdot CO_2H$, which is produced by spontaneous oxidation of the aldehyde, is transformed into the stereoisomeric *iso*camphenilanic acid when heated with concentrated nitric acid. Our experiments show that if bornylene is subjected to the action of chromyl chloride dissolved in carbon disulphide, it also yields a solid *additive product*, $C_{10}H_{16},2CrO_2Cl_2$, which reacts easily with water, but, unlike the corresponding camphene compound, gives two products. One of these, a saturated *chloro-ketone*, $C_{10}H_{15}OCl$, which constitutes about 65 per cent. of the whole, is apparently a derivative of camphor; the other is camphenilanaldehyde, a substance which has already been prepared from camphene in several different ways, and of which the formation from bornylene is of great interest. The aldehyde is probably mixed with a little *iso*camphenilanaldehyde, which has been obtained from camphene in a different manner (Henderson and Sutherland, this vol., p. 1539), because the acid

formed by its spontaneous oxidation in the air appears to contain a small proportion of *iso*camphenilanic acid. If, as is probable, camphenilanaldehyde has the formula given below (III), its formation from bornylene (I) must involve a certain rearrangement of the latter's molecular structure. Possibly an unstable oxide (II) is produced by the action of water on the additive compound, and at once changes to the aldehyde:



(I.) (II.) (III.)

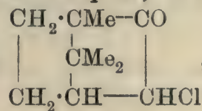
It is most probable that camphenilanic and *iso*camphenilanic acids are stereoisomerides, and, as Bredt and Jagelki have shown, the *iso*-acid is produced when the other is subjected to prolonged heating with nitric acid, or when camphenilanaldehyde is oxidised with potassium permanganate. We have found that repeated slow crystallisations from such solvents as water, alcohol, and light petroleum likewise bring about the conversion of the one form into the other, although the process is tedious and incomplete; quite a number of different mixtures of the two acids which have constant melting points can be obtained by rapid crystallisation. From acetic acid, on the other hand, camphenilanic acid can be crystallised several times with little or no formation of the *iso*-acid. We have also observed that on treatment with semicarbazide hydrochloride and potassium acetate in the usual manner, camphenilanaldehyde yields the semicarbazone of *iso*camphenilanaldehyde, which, when liberated by the action of dilute acids, is converted into the *iso*-acid on exposure to the air.

For comparison with bromocamphenilanic acid, we prepared *bromo*iso*camphenilanic acid*, $C_9H_{14}Br\cdot CO_2H$, by converting the *iso*-acid into its *chloride*, $C_9H_{15}\cdot COCl$, heating this compound with bromine under pressure at about 60°, and decomposing the product, the *chloride* of bromo*iso*camphenilanic acid, $C_9H_{14}Br\cdot COCl$, with water. If the bromination of the chloride is carried out at a higher temperature, a crystalline neutral compound, which appears to have the formula $C_{10}H_{15}OBr$, is produced along with the bromo-acid. On one occasion we used *iso*camphenilanic acid mixed with a considerable proportion of camphenilanic acid, in the expectation of obtaining a mixture of the bromo-acids which might be more easily separated than the parent substances. The sole product, however, was bromo*iso*camphenilanic acid, and it is evident that during the process the chloride of camphenilanic or of bromocamphenilanic acid must have undergone conversion into the corresponding derivative of *iso*camphenilanic acid.

When heated with aqueous sodium carbonate, bromocamphenilanic acid yields the α-hydroxy-acid, camphenylic acid,

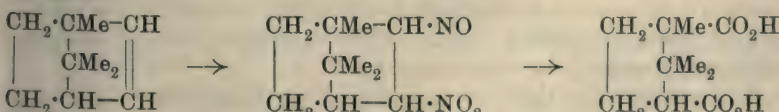
$$C_9H_{14}(OH)\cdot CO_2H,$$

but bromo*iso*camphenilanic acid behaves quite differently, being converted into an unsaturated acid, $C_9H_{13}\cdot CO_2H$.

The chloro-ketone, $C_{10}H_{15}OCl$, forms a *semicarbazone*, which melts and decomposes at 234—235°. The chlorine in the ketone is not easily displaced, but on heating the compound with concentrated alcoholic potassium hydroxide under pressure at 160° it is converted into camphor, and it is slowly oxidised to camphoric acid by treatment with an alkaline solution of potassium permanganate. The compound, therefore, is a *chlorocamphor*, and possibly is stereoisomeric with 3-chlorocamphor, , which melts at 93—94°.

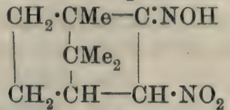
The formation of camphenilanaldehyde, a derivative of camphene, from bornylene is of considerable importance, as indicating that there is great similarity between the nuclei of these terpenes. The results of the investigation of other derivatives of these terpenes, which we hope to be able to communicate to the Society before long, appear to support this view.

Results which are of importance as regards the question of its constitution have been obtained by subjecting camphene to the action of nitrous and nitric acids, and it therefore appeared of interest to investigate the behaviour of bornylene when attacked by these reagents. From camphene, by treatment with nitrous acid, Jagelki (*Ber.*, 1899, **32**, 1498) obtained a crystalline nitronitrosite, $C_{10}H_{15}(NO_2)(N_2O_3)$, and an oily *iso*nitrosite, $C_{10}H_{16}(N_2O_3)$, which was readily decomposed, yielding the so-called camphenil nitrite, $C_{10}H_{15}\cdot NO_2$; the latter compound was easily converted into camphenilanaldehyde, $C_{10}H_{16}O$, and camphenilone, $C_9H_{14}O$, respectively. When treated in a similar manner with nitrous acid, bornylene has been found to yield several different compounds, some of which differ essentially in character from the derivatives obtained from camphene. The chief product was a crystalline *nitrosite*, $C_{10}H_{16}(N_2O_3)$, which proved to be bimolecular, and evidently has the same nucleus as bornylene, because it yields camphoric acid on oxidation:



Another product was a viscous liquid of a green colour, which

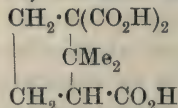
owing to its extreme instability could not be purified sufficiently for analysis. It is very similar in properties to the *iso*nitrosite prepared from camphene, for example, in its solubility in aqueous solutions of alkali hydroxides, and in all probability is the corresponding *bornylene* iso*nitrosite*,



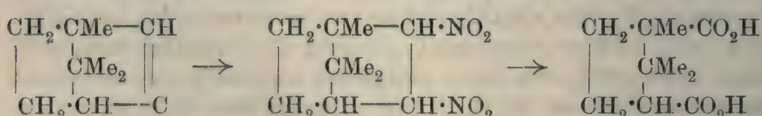
.

In addition to the above, we found among the products of the reaction a considerable quantity of a crystalline solid, melting at 198°, which was proved to be camphorquinone, and a very small amount of a colourless, crystalline compound, which melted at 84—85°. This substance contains nitrogen, but the quantity in our hands was too small to permit of its identification.

On oxidising camphene with nitric acid, Marsh and Gardner (Trans., 1891, **59**, 648; 1896, **69**, 74) obtained the tribasic camphoic (carboxy*apo*camphoric) acid,



. When bornylene was oxidised in a similar manner, we found, as was to be expected, that the chief product was camphoric acid. Along with this there separated from the mixture of oxidation products a yellow, crystalline compound, which melts at 137°, and volatilises in a current of steam. This compound proved to be a *dinitrocamphane*, $C_{10}H_{16}(NO_2)_2$, and its formation must be due to the addition of nitric peroxide, produced by reduction of the nitric acid, to some of the bornylene. On oxidation with dilute alkaline permanganate, it is readily converted into camphoric acid:



On reduction with sodium and alcohol, or with tin and hydrochloric acid, this dinitrocamphane is completely decomposed, but alcoholic ammonium sulphide converts it into a yellow, crystalline substance, which is apparently not an amino-derivative, but possibly a mononitrocamphane.

Besides these substances the mixture of products was found to contain a very small quantity of a colourless, crystalline compound, which melts at about 174°. This compound, which contains nitrogen, is neutral in character.

Our results show that neither nitrous nor nitric acid, when used under the conditions described below, tends to bring about any

rearrangement of the nucleus of bornylene, for the products are all typical derivatives of that hydrocarbon, and not of camphene.

We are at present engaged in studying other derivatives of bornylene, and shall submit our results to the Society before long.

Experimental.

The Oxidation of Bornylene with Chromyl Chloride.

Preparation and Oxidation of Bornylene.—Bornylene was prepared from borneol, through bornyl methyl xanthate, essentially according to the method of Tschugaeff (*Ber.*, 1899, **32**, 3332), but with modifications which experience has shown to be of value. In the first stage of the process the best results were obtained by boiling a solution of 200 grams of borneol in 250 grams of dry toluene with the necessary quantity of sodium. The heating of the liquid was effected by means of a glycerol bath, because when a sand-tray is used, local overheating and consequent charring through decomposition of the material are apt to occur, and there is considerable risk of the flask breaking.

A 10 per cent. solution of 100 grams of chromyl chloride (2 mols.) in dry carbon disulphide was slowly added, in small portions, to a well-cooled solution of 44 grams of bornylene (1 mol.) in the same solvent and of similar concentration, with thorough agitation after each addition. The reaction proceeded smoothly, with evolution of heat, and a dark brown precipitate slowly settled, and was then collected, washed with carbon disulphide, and transferred to wide-mouthed bottles while still in the form of a pasty mixture with some of the solvent. The mass was added, in small quantities at a time, to ice-cold water containing a little sulphurous acid, and the mixture vigorously shaken after each addition until the solid was completely decomposed, with the result that an oily substance separated from the aqueous solution. The oxidation product was extracted by repeated agitation of the mixture with carbon disulphide, and the extract was well washed with water, dried with calcium chloride, and heated to expel the carbon disulphide. The yield is very good, little or no resinification taking place.

The *additive compound*, $C_{10}H_{16},2CrO_2Cl_2$, thus obtained from bornylene is, when in the dry state, a light brown powder. It is extremely hygroscopic, and decomposes on exposure to moist air, forming a dark green liquid with a sweet odour.

Separation and Identification of Camphenilanaldehyde.—The oily liquid obtained from the additive product was well mixed with a saturated solution of sodium hydrogen sulphite, with the result that after some time a crystalline "bisulphite compound" separated in

very small, colourless plates. Ether was added in order to extract the substance which had not reacted with the bisulphite, and the ethereal solution was separated and treated with fresh quantities of the reagent until no more of the bisulphite compound was formed. The crystals were collected, and washed with alcohol and with ether, and the aqueous filtrate was extracted with ether, this ethereal solution being added to the first. The bisulphite compound was mixed with aqueous sodium carbonate, and heated with steam, and the aldehyde which solidified in the receiver was collected, quickly dried by pressure in porous paper, and distilled in an atmosphere of dry carbon dioxide. In this way the aldehyde was obtained in colourless crystals, with a strong odour. It melted at 71—72°, boiled at 192—193° under atmospheric pressure, and was quickly oxidised on exposure to the air. Its semicarbazone was prepared, and purified by crystallisation from methyl alcohol, from which it separated in lustrous, pearly leaflets, with the melting point 191—192°. (Found, C=63·1; H=9·1; N=20·3. Calc., C=63·1; H=9·1; N=20·1 per cent.)

As the properties of this aldehyde from bornylene appeared to be identical with those of Bredt's camphenilanaldehyde, we prepared a quantity of the latter from camphene for purposes of comparison, and converted some of it into its semicarbazone. (Found, N=20·2.)

This semicarbazone melted at the same temperature as that prepared from the aldehyde obtained from bornylene, and the melting point remained unaltered when the two compounds were mixed. In short, bornylene, when oxidised with chromyl chloride, yields the same aldehyde as camphene does when similarly treated.

We observed also that the semicarbazones prepared from camphenilan- and *iso*camphenilan-aldehydes, as also a mixture of the two, have the same melting point. To clear up this point we decomposed some of the semicarbazone prepared from camphenilanaldehyde by warming it with the calculated quantity of dilute sulphuric acid, and found that the liberated aldehyde was wholly oxidised to *iso*camphenilanic acid on exposure to the air. Hence it appears that the product of the action of semicarbazide hydrochloride on camphenilanaldehyde is the semicarbazone of *iso*camphenilanaldehyde—a result which is not surprising, because the two aldehydes are almost certainly stereoisomerides.

Camphenilanic and iso*Camphenilanic Acids.*—The aldehyde obtained from bornylene was exposed to the air for some time, and, after oxidation appeared to be complete, the acid formed was separated from any unchanged aldehyde by means of aqueous sodium carbonate. Acidification of the alkaline solution produced an oily precipitate, which soon solidified, and was then collected,

washed with water, and dried. A melting-point determination showed that, whilst the bulk of the product was camphenilanic acid, a small proportion of an acid of higher melting point was also present. By fractional crystallisation from somewhat diluted acetic acid the camphenilanic acid was obtained in crystals melting at 65°; the other acid separated from light petroleum or from dilute alcohol in colourless prisms, which melted at 118°, and in all other respects was exactly similar to *iso*camphenilanic acid. Analysis established its identity. (Found, C = 71·6; H = 9·3. Calc., C = 71·4; H = 9·5 per cent.)

Having accumulated a quantity of camphenilanic acid, we endeavoured to convert it into its isomeride by crystallisation from different solvents, and found that when repeatedly crystallised from water, alcohol, or light petroleum, camphenilanic acid is gradually transformed into *iso*camphenilanic acid. For example, a specimen of the former acid which melted at 65°, after one crystallisation from water melted at 70°, and after a second at 86°. The process is tedious and unsatisfactory owing to the tendency of the two acids to form mixtures of constant melting point, and the consequent difficulty in separating them. *iso*Camphenilanic acid is not formed when camphenilanic acid is crystallised from glacial acetic acid, or heated at a temperature above its melting point for several days, or exposed to ultra-violet light. Bredt showed that the *iso*-acid is produced when camphenilanic acid is boiled with concentrated nitric acid, but according to our experience some of the latter remains unaltered, even when the heating is prolonged for a fortnight. A mixture of the two acids was also obtained when camphenilanaldehyde was oxidised with an alkaline solution of potassium permanganate. A comparatively simple method of obtaining *iso*camphenilanic acid is to convert camphenilanaldehyde into the semicarbazone, to decompose this compound with dilute acids, and to allow the *iso*camphenilanaldehyde thus produced to undergo oxidation in the air.

*Preparation of Bromo*iso*camphenilanic Acid and of the Unsaturated Acid* $C_9H_{13}\cdot CO_2H$.—The *chloride* of iso*camphenilanic acid*, $C_9H_{15}\cdot COCl$, was prepared by adding the acid in small portions to a mixture of the calculated quantity of phosphorus pentachloride with light petroleum, heating under a reflux condenser until the reaction was completed, and finally distilling fractionally under diminished pressure. The chloride is a colourless, oily liquid, with a not unpleasant odour, which boils at 118°/25 mm., and rapidly decomposes in moist air, with formation of *iso*camphenilanic acid. By heating in a sealed tube for several hours at about 60° with a slight excess of bromine it was converted into the *chloride* of *bromo-*

*iso*camphenilanic acid, $C_9H_{14}Br{\cdot}COCl$, which is also a heavy, viscous liquid, and is decomposed by water, giving *bromo*iso*camphenilanic acid*, $C_9H_{14}Br{\cdot}CO_2H$. The chloride was poured into water, and the mixture well stirred until the oily chloride was completely converted into the crystalline acid, which was collected, washed with water, and purified by recrystallisation, first from dilute methyl alcohol, and finally from light petroleum. The acid forms small, colourless prisms, which melt at 204—205°. It is readily soluble in alcohol, ether, or light petroleum, but almost insoluble in water:

0·2022 gave 0·1550 AgBr. Br = 32·6.

$C_{10}H_{15}O_2Br$ requires Br = 32·3 per cent.

In the first preparation of bromo*iso*camphenilanyl chloride the mixture was heated in a sealed tube at 100° for about twenty-four hours. On treatment of the product with water, a mixture of bromo*iso*camphenilanic acid with a considerable proportion of a neutral compound, $C_{10}H_{15}OBr$, was obtained. This substance crystallises from methyl alcohol in minute, colourless needles, which melt at 182°. It is sparingly soluble in methyl alcohol, readily so in ether or light petroleum, and insoluble in water and in aqueous solutions of sodium carbonate or sodium hydroxide:

0·2076 gave 0·1687 AgBr. Br = 34·6.

$C_{10}H_{15}OBr$ requires Br = 34·6 per cent.

With the object of preparing the corresponding hydroxy-derivative, bromo*iso*camphenilanic acid was warmed for about three hours on the water-bath with aqueous sodium carbonate. From the solution, on cooling, a rather sparingly soluble sodium salt crystallised out. The salt was dissolved in water and decomposed by addition of dilute sulphuric acid, and the precipitated acid was purified by crystallisation from dilute methyl alcohol. Examination of this substance proved it to be, not the expected hydroxy-acid, but an unsaturated *acid* of the formula $C_9H_{13}{\cdot}CO_2H$. It crystallises in fine, lustrous plates, melts at 147°, is readily soluble in alcohol or ether, but insoluble in water, and volatilises in a current of steam. It immediately reduces an alkaline solution of potassium permanganate in the cold:

0·1855 gave 0·4878 CO_2 and 0·1480 H_2O. C = 71·7; H = 8·8.

$C_{10}H_{14}O_2$ requires C = 72·2; H = 8·4 per cent.

The *sodium* salt, $C_9H_{13}{\cdot}CO_2Na$, separates from water, in which it is not very readily soluble, in beautiful, silky plates.

Separation of the Chloro-ketone, $C_{10}H_{15}OCl$.—The ethereal solution of the oxidation product, from which the aldehyde had been removed by treatment with sodium hydrogen sulphite, was washed successively with aqueous sodium carbonate and with water, and

dried. The ether was removed by distillation, the residue heated in a current of steam, and the yellow solid, which condensed in the receiver, collected and pressed on a porous plate to remove traces of oily matter. Purification of this substance by crystallisation was difficult, owing to its great solubility in all the usual organic solvents, and the method finally adopted was repeated fractional precipitation with water from a solution in glacial acetic acid. Once partly purified in this way the substance can be crystallised from dilute alcohol. When pure it forms minute, colourless crystals, which melt sharply at 165°, and have a faint, pleasant odour. It is extremely volatile in steam, but decomposes on distillation, even under diminished pressure. Its solubility in organic solvents is very great, but it is insoluble in water. It has the character of a saturated ketone, readily forming a semicarbazone, but resisting oxidation:

0·2218 gave 0·5230 CO_2 and 0·1610 H_2O. C = 64·3; H = 8·1.
0·1636 ,, 0·1256 AgCl. Cl = 19·0.
$C_{10}H_{15}OCl$ requires C = 64·3; H = 8·1; Cl = 19·0 per cent.

The *semicarbazone* of the *chloro-ketone*,

$$C_{10}H_{15}Cl{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

which was prepared in the usual way, crystallises from dilute alcohol in small, colourless prisms. It is fairly readily soluble in alcohol, and melts at 234—235°, beginning to decompose a little below this temperature:

0·1850 gave 28·6 c.c. N_2 (moist) at 14° and 758 mm. N = 18·2.
$C_{11}H_{18}ON_3Cl$ requires N = 17·3 per cent.

The chloro-ketone was found to be slowly oxidised by potassium permanganate in alkaline solution. After heating on the water-bath for two days, the excess of permanganate was reduced with sulphurous acid, the precipitated manganese dioxide removed by filtration, and the filtrate concentrated to small bulk. On addition of dilute sulphuric acid a crystalline acid was obtained, and was collected and recrystallised from hot water. The purified acid melted at 187°, and in other respects resembled camphoric acid. Its identity was established by heating it at a temperature above its melting point in a current of carbon dioxide, distilling the product, and recrystallising the distillate from alcohol. The crystals melted sharply at 221°, the melting point of camphoric anhydride.

The removal of chlorine from the ketone was difficult, and attempts to effect this by heating it with silver oxide in alcoholic solution and by treatment with sodium and alcohol proved fruitless. The end was attained by heating 5 grams of the ketone with a concentrated alcoholic solution of 2 grams of potassium hydroxide in a sealed tube for seven hours at 150—160°. The alcoholic

solution was mixed with water and agitated several times with ether, and the ethereal extract was washed with water, dried, and distilled to remove the ether. The residue was heated in a current of steam, and a crystalline solid separated from the distillate, which in all respects was indistinguishable from camphor. The solid was converted into a semicarbazone, which after crystallisation from methyl alcohol melted at 236°, the melting point of camphorsemicarbazone, and from which, by treatment with dilute sulphuric acid, a specimen of camphor, melting at 174°, was regenerated.

From these results it is evident that the chloro-ketone is a *chlorocamphor*, different from any hitherto described.

The Action of Nitrous Acid on Bornylene.

Preparation of the Nitrosite.—Glacial acetic acid was added very slowly, in small quantities at a time, to a concentrated aqueous solution of 100 grams of sodium nitrite, on which rested a concentrated solution of 100 grams of bornylene in light petroleum. The mixture was gently warmed on the water-bath under a reflux condenser, with occasional agitation, for about an hour, and then left for twenty-four hours at the ordinary temperature. During this time crystals of the nitrosite slowly separated at the surface of the aqueous layer, the light petroleum acquiring, first a blue, then an intense green, and finally, at the end of the reaction, a yellow coloration. The petroleum solution was removed, and repeatedly treated in the same manner with fresh quantities of sodium nitrite and acetic acid until the odour of bornylene had disappeared. This method gave better results than prolonged treatment of bornylene with nitrous acid in one operation. The crystals of the nitrosite were separated from the aqueous solution by filtration through glass wool, thoroughly washed with water, alcohol, and ether successively, and purified by crystallisation from acetone. From this solvent the nitrosite separates in beautiful, silky needles, which, when quickly heated, melt sharply at 163°, forming a bluish-green liquid, which decomposes with violent gas evolution. It is readily soluble in acetone, glacial acetic acid, benzene, or chloroform, but very sparingly so in alcohol or ether, and is insoluble in water or aqueous solutions of alkali hydroxides or hydrochloric acid. The solutions have a characteristic blue colour. The nitrosite is not decomposed by alkali hydroxides or concentrated hydrochloric acid, even when heated:

0·2044 gave 0·4176 CO_2 and 0·1470 H_2O. C = 55·7; H = 8·0.
0·2055 ,, 24 c.c. N_2 (moist) at 13·2° and 740 mm. N = 13·4.

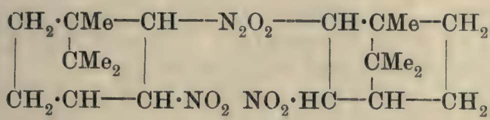
$C_{10}H_{16}O_3N_2$ requires C = 56·6; H = 7·5; N = 13·2 per cent.

Determinations of the molecular weight by the ebullioscopic method in acetone solution gave the following results:

Substance (gram).	Solvent (grams).	E.	M.W.
0·2196	17·47	0·05°	432
0·4291	17·47	0·118°	358
0·6495	17·47	0·185°	346

$C_{10}H_{16}O_3N_2$ requires M.W. = 212.

These results indicate that the substance is bimolecular, the fall in the molecular weight in the later determinations being possibly due to a slight decomposition of the complex molecule on continued heating of the solution. The bimolecular form may be represented thus:



The nitrosite, on oxidation with a warm dilute alkaline solution of potassium permanganate, yields an acid, which melts at 187°, and in all other respects is identical with camphoric acid.

Separation of the iso*Nitrosite*.—The light petroleum, from which the nitrosite had separated, was repeatedly agitated with concentrated aqueous potassium hydroxide until nothing more passed into solution, and the red alkaline liquid was diluted with water and acidified with hydrochloric acid, care being taken to keep the mixture cool. The liquid was repeatedly agitated with ether, the ethereal extract washed with water and dried, and, after removal of the ether by distillation, the iso*nitrosite* was obtained as a viscid, oily liquid, with a green colour and a pleasant odour. It is an extremely unstable substance, decomposing with violent evolution of gas when heated, even under greatly diminished pressure. It dissolves in aqueous solutions of alkali hydroxides, and the alkali derivatives are extremely readily soluble in all solvents. A small quantity of the *potassium* salt, probably $C_{10}H_{15}\cdot N_2O_3K$, was obtained as an orange-coloured powder by the action of potassium ethoxide on a solution of the *iso*nitrosite in dry benzene. Attempts to prepare products of hydrolysis and of reduction of the *iso*nitrosite were unsuccessful, as in each case the substance was apparently completely decomposed; yet its close resemblance to the corresponding *iso*nitrosite prepared from camphene lends probability to the conclusion that this compound is bornylene *iso*nitrosite.

Separation of Camphorquinone.—After extraction of the *iso*nitrosite by aqueous potassium hydroxide, the petroleum solution was well washed with water, dried, and, after removal of the light petroleum by distillation, the residual yellow oil was fractionated

under diminished pressure. The most volatile fraction consisted of some bornylene which had escaped attack, and the second fraction, which was small in quantity, had a strong odour of camphor; the last fraction, which had a deep yellow colour, deposited some crystals on keeping. After removal of these crystals, the yellow, oily liquid which remained was placed in the ice-chest, when it gradually solidified, and after purification by crystallisation from light petroleum was obtained in delicate needles, of a deep yellow colour and with a strong odour, which melted sharply at 197—198°. It is readily soluble in organic solvents, and sparingly so in hot water; it volatilises very easily in a current of steam, and sublimes readily at a low temperature. In all these respects it is identical with camphorquinone. The aqueous solution, from which the crystals of nitrosite had been separated by filtration, had a deep yellow colour, and also yielded some camphorquinone.

The crystalline solid, which separated from the distillate of crude camphorquinone, melted at 70—80°, and was evidently a mixture of the latter with some other substance. By repeated crystallisation of this mixture from methyl alcohol this compound was obtained in colourless prisms, which melted at 84—85°. It is sparingly soluble in water, and readily so in organic solvents. Analysis gave results which indicated that the substance might be bornylene nitrite, but we were unable, from lack of material, to confirm this. On treatment with alkali it yields a substance which resembles camphor:

0·1984 gave 0·4866 CO_2 and 0·1774 H_2O. C = 66·9; H = 9·9.
0·1472 „ 9·95 c.c. N_2 (moist) at 24° and 777 mm. N = 7·7.
$C_{10}H_{15}O_2N$ requires C = 66·2; H = 8·3; N = 7·7 per cent.

The Action of Nitric Acid on Bornylene.

Separation of Dinitrocamphane.—Forty grams of bornylene were warmed on the water-bath under a reflux condenser with about 500 c.c. of 30 per cent. nitric acid. Vigorous action took place, nitrous fumes being evolved in quantity, whilst owing to the heat of the reaction some of the unattacked bornylene volatilised into the tube of the condenser. After about an hour, when the first action had ceased, the flask and its contents were allowed to cool, and a further quantity of 270 c.c. of nitric acid (D 1·4) was added very gradually in small portions at a time. Care must be taken at this stage, for if too much of the strong acid was added at once oxidation took place with almost explosive violence. During this part of the process the bornylene which had volatilised was attacked by the nitric acid and the nitrous fumes, and washed back

into the flask. After all visible action had ceased, the solution was boiled in order to expel nitrous fumes, and left for twelve hours at the ordinary temperature, when a mass of crystals was deposited. The crystals were separated from the strongly acid liquid by filtration through glass wool, well washed with water, and dried in porous paper. Inspection revealed the presence of two substances in the product, some of the crystals being yellow and others colourless. The colourless crystals were found to be soluble in aqueous sodium carbonate, and therefore the mixture was warmed with excess of this reagent and the alkaline solution repeatedly shaken with ether, in which the yellow substance dissolved. The ethereal solution was washed with water, dried, and, after removal of the ether by distillation, a yellow, oily substance was obtained, which became crystalline on keeping. After purification by crystallisation from methyl alcohol, this substance, 1:2-*dinitrocamphane*, had the form of long, slender, pale yellow needles, which melted at 137° without any signs of decomposition. It is readily soluble in ether or chloroform, moderately so in methyl or ethyl alcohol, and insoluble in water or acids. It dissolves to a small extent in hot solutions of the alkali hydroxides, imparting a deep yellow colour to the liquid. It volatilises slowly in a current of steam. Towards bromine or potassium permanganate the compound is inactive, being evidently saturated. The yield was about 5 per cent. of the bornylene taken. Analysis showed that it had the composition of a dinitrocamphane:

0·2033 gave 0·3916 CO_2 and 0·1320 H_2O. C = 52·6; H = 7·2.
0·2363 „ 26·4 c.c. N_2 (moist) at 16° and 737 mm. N = 12·4.
$C_{10}H_{16}O_4N_2$ requires C = 52·6; H = 7·0; N = 12·3 per cent.

When warmed with a dilute alkaline solution of potassium permanganate, the yellow crystals of the dinitrocamphane were gradually oxidised, and passed into solution. After the oxidation was completed, the precipitated manganese dioxide was removed by filtration, the filtrate acidified, and the acid which separated collected and crystallised from boiling water. It then melted at 187°, and was proved to be camphoric acid by conversion into camphoric anhydride, melting at 221°.

The ready oxidation of the substance to camphoric acid, and the results of analysis, prove that it has the bornylene or camphane structure, and is in all probability a dinitrocamphane, but attempts to prepare the corresponding diamino-derivative were unsuccessful. When sodium and alcohol or tin and hydrochloric acid were used as the reducing agent, complete disintegration of the molecule took place, gaseous fatty amines being evolved, and no definite product was obtained. Reduction with ammonium sulphide, on the other

hand, yielded a well-characterised compound. The dinitrocamphane was dissolved in alcohol, the necessary quantity of a concentrated solution of ammonia added, and hydrogen sulphide passed into the solution for some time. During this operation the liquid, previously almost colourless, acquired a dark red colour. The solution was then boiled for half an hour, filtered to remove precipitated sulphur, and left to cool, when crystals of a deep yellow colour separated. After recrystallisation from alcohol, the new compound was obtained in minute, hard prisms of a canary-yellow colour, which melt at 196—198°. It is only sparingly soluble in alcohol, and insoluble in water, but dissolves readily in ether. The quantity at our disposal only permitted of a nitrogen estimation. The result suggested that the new compound may be a mononitrocamphane, but it remains to be proved whether or not this is the case:

0·2026 gave 13·5 c.c. N_2 (moist) at 19° and 763 mm. N = 7·7.

$C_{10}H_{17}O_2N$ requires N = 7·6 per cent.

Separation of Camphoric Acid.—As already stated, colourless crystals of an acid separated along with the dinitrocamphane from the acid solution in which the bornylene had been oxidised, and were removed by treatment of the mixture with aqueous sodium carbonate. A further quantity was obtained from the acid mother liquor, which was subjected to steam distillation in order to remove a little dinitrocamphane which remained in solution, rendered alkaline by addition of excess of sodium carbonate, and agitated with ether, which dissolved a little of a substance which separated when the acid was neutralised. The mixed alkaline solutions were concentrated, and on acidification yielded a large quantity of an acid. After recrystallisation from water the acid melted at 187°, and its identity with camphoric acid was proved by analysis. (Found, C = 60·2; H = 8·1. Calc., C = 60·0; H = 8·0 per cent.)

The ethereal solution of the substance extracted from the alkaline liquid was washed and dried, and after removal of the ether a viscous, oily substance remained. This was distilled under diminished pressure in an atmosphere of dry carbon dioxide; considerable decomposition took place, but a portion which distilled at 180—185°/25 mm. solidified on cooling to a yellow mass. After repeated crystallisation from light petroleum the compound was obtained in the form of minute, colourless needles, which melted at about 174°. It is very readily soluble in alcohol, ether, or acetone, somewhat sparingly so in light petroleum, and insoluble in water, alkalis, or dilute mineral acids. The yield of this compound is extremely small, and from several different preparations only enough for one analysis was obtained, according to which the compound contains C = 71, H = 10, and N = 6·7 per cent.

We take this opportunity of thanking Mr. D. S. Dawson, B.Sc., and Mr. William Caw for valuable assistance, and the Carnegie Trust for a grant in aid of the expense of this work.

CHEMISTRY DEPARTMENT,
THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

CCXIV.—*The Constitution of Camphene.*

By GEORGE GERALD HENDERSON and ISIDOR MORRIS HEILBRON.

THERE is still room for difference of opinion regarding the constitution of camphene, but this at least is certain, that the formula originally assigned to this terpene by Bredt is in reality that of the closely related bornylene (I), as is shown by the formation of the latter from borneol (II) through bornyl methyl xanthate, and by the ease with which it is converted into camphoric acid by oxidation. There can also be little doubt that the nuclei of camphene and bornylene, although to a large extent similar in structure, differ from one another more widely than, for example, in the position of a double linking, because, among other reasons, it has been observed that, on reduction by the contact method of Sabatier and Senderens, bornylene readily yields camphane, whilst camphene is converted into a dihydro-derivative which is quite different from camphane (Henderson and Pollock, Trans., 1910, **97**, 1620). It is generally agreed that bornylene is the normal product from borneol, and therefore that the formation of camphene from this alcohol is attended by a certain structural rearrangement.

From camphene, by the action of chromyl chloride, Bredt and Jagelki (*Annalen*, 1900, **310**, 112) obtained an additive compound which on treatment with water gave only one product, camphenilanaldehyde (V). From the corresponding acid an α-hydroxy-derivative, camphenylic acid (VI), was prepared, and from the latter, by oxidation, the ketone camphenilone (VII), which so closely resembles camphor both in physical and in physiological properties. By means of an entirely different oxidising agent, hydrogen peroxide, Henderson and Sutherland (this vol., p. 1539) recently obtained from camphene a mixture of oxidation products, the chief of which were *iso*camphenilanaldehyde (which is almost certainly a stereoisomeride of camphenilanaldehyde), camphenilone, and an acid, $C_{10}H_{16}O_2$, isomeric with *iso*camphenilanic acid, into which it is transformed when heated with acetic anhydride. Camphene has also been converted into camphenilanaldehyde or camphenilone respec-

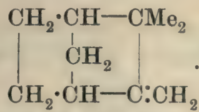
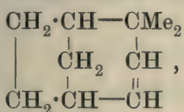
tively in other direct and simple ways; thus, when camphene nitrite (VIII) is hydrolysed, it yields the aldehyde, through rearrangement of the unsaturated alcohol (IX), which is the direct product of hydrolysis, while camphenilone is produced when the nitrite is treated with a dilute solution of potassium permanganate (Jagelki, *Ber.*, 1899, **32**, 1498). Further, in the course of an elaborate investigation of the products obtained by oxidising camphene with a dilute aqueous solution of potassium permanganate, Moycho and Zienkowski (*Annalen*, 1905, **340**, 17) prepared camphene glycol (IV) in considerable quantity, and showed that this compound must contain two hydroxyl groups, although it only yields a monobenzoate, and that all its reactions point to the formula,

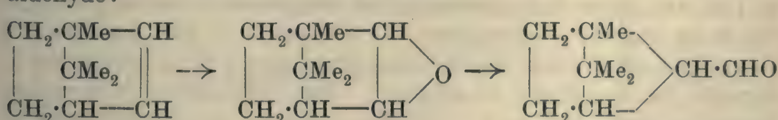
$$C_8H_{14}{:}C(OH){\cdot}CH_2{\cdot}OH.$$

They found that camphenilanaldehyde was formed from the glycol under such conditions that no structural rearrangement would take place, and therefore that the linking of the carbon atoms in the two compounds is the same. Camphenylic acid and camphenilone were identified among the other products of the oxidation of the camphene, and were also prepared from the pure glycol by treatment with permanganate. Moycho and Zienkowski consider that their results prove conclusively the presence of the group $>C{:}CH_2$ in the molecule of camphene, and this view is supported by the observation of Balbiano and Paolini (*Ber.*, 1903, **36**, 3375) that camphene yields an additive compound when treated with aqueous mercuric acetate, whereas, according to these observers, the presence of a $\cdot CH{:}CH\cdot$ group would lead to the formation of an oxidation product.

The formation of camphenilanaldehyde from camphene by such different methods as those quoted, indicates that the central nucleus and the mode of attachment of the side groups in each of the two substances are identical. Definite proof of this has been given by Semmler (*Ber.*, 1909, **42**, 246, 962), who converted the aldehyde into an *enol*-acetate, reduced the latter to camphenilyl alcohol, prepared the corresponding chloride, and from this, by treatment with sodium and alcohol, regenerated camphene. It is also known that camphenilone has the same nucleus as camphene, for not only is it produced when the hydrocarbon is oxidised with potassium permanganate, or with hydrogen peroxide, or with moist ozone, but, in addition, the direct synthesis of camphene from camphenilone, through methylcamphenilol, has been effected by Moycho and Zienkowski (*Ber.*, 1905, **38**, 1061).

The formation and relationships of the derivatives mentioned above can be explained if the constitution of camphene be repre-

sented by the formula  . This formula was suggested by Wagner as the result of his study of the alcohols borneol and *iso*borneol, which, as corresponding with bornylene and camphene respectively, were believed to have quite different structures. But although borneol is a secondary, and *iso*borneol apparently a tertiary alcohol, it seems difficult to reconcile the view that their nuclei are entirely different with the facts that *iso*borneol on oxidation yields camphor, a ketone with the same nucleus as borneol, that under suitable conditions camphene can be obtained from borneol, and that *iso*borneol is converted into the sodium derivative of borneol when heated with sodium in xylene solution. If camphene had the constitution expressed in Wagner's formula, or in the formula  , which has been tentatively proposed by Aschan in a recent paper (*Annalen*, 1910, **375**, 336), its formation from borneol would involve a greater rearrangement of the molecule than seems probable from the facts already quoted, and, moreover, observations recently made in this laboratory (Henderson and Heilbron, this vol., p. 1887) indicate that the molecular structure of camphene is closely related to that of bornylene. It has been found that, on treatment with chromyl chloride, bornylene gives an additive product, from which, by the action of water, excellent yields of two substances are obtained. One of these, a chloro-ketone of the formula $C_{10}H_{15}OCl$, appears to be a chlorocamphor, while the other is a derivative of camphene, being, in fact, camphenilan-aldehyde. If the formula of the aldehyde is that given below, the formation of this camphene derivative from bornylene can be easily understood, for it is only necessary to assume that when the additive compound reacts with water a substance of the type of an oxide is formed, which by a slight rearrangement passes into the aldehyde:



Bornylene. Camphenilanaldehyde.

Such a rearrangement of the bornylene molecule is insignificant compared with that which would be involved if camphene were constituted as represented in the formulæ of Wagner or of Aschan.

These results lead to the conclusion that as regards the greater part of their respective molecules, namely, the residue,

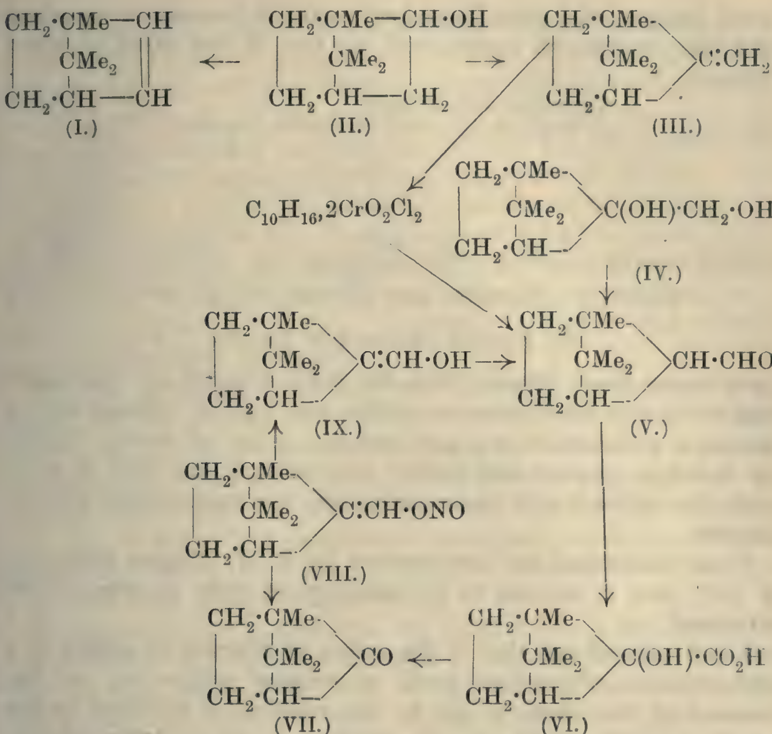
$$\begin{array}{l} CH_2\cdot CMe\cdot \\ \Big| \qquad \ \ | \\ \Big| \qquad CMe_2\ , \\ \Big| \qquad \ \ | \\ CH_2\cdot CH\cdot \end{array}$$

camphene and bornylene are identical. Support is given to this conclusion by the fact that camphene resembles bornyl chloride, which also contains this residue, in yielding camphor on oxidation with chromate mixture, and also, to a less extent, by the observation of Marsh and Gardner (Trans., 1891, **59**, 648; 1896, **69**, 74) that camphene is oxidised by moderately dilute nitric acid to camphoic (carboxy*apo*camphoric) acid, which on heating loses carbon dioxide and forms *apo*camphoric acid, which has been synthesised by Komppa (*Ber.*, 1901, **34**, 2472):

$$\begin{array}{l} CH_2\cdot C(CO_2H)_2 \\ \Big| \qquad \ \ | \\ \Big| \qquad CMe_2 \\ \Big| \qquad \ \ | \\ CH_2\cdot CH\cdot CO_2H \end{array} \longrightarrow \begin{array}{l} CH_2\cdot CH\cdot CO_2H \\ \Big| \qquad \ \ | \\ \Big| \qquad CMe_2 \\ \Big| \qquad \ \ | \\ CH_2\cdot CH\cdot CO_2H \end{array} .$$

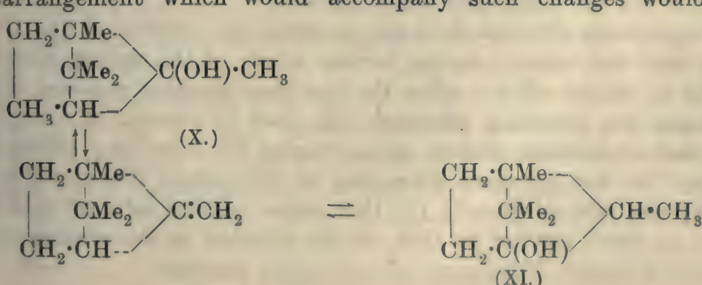
The relationship of all the derivatives of camphene, which have been mentioned above, to the present hydrocarbon and to each other can be stated very simply, as is shown in the scheme on p. 1905, on the assumption that camphene has the formula (III), which was originally proposed by Semmler, and which we consider to be the best expression of the known facts.

It must be noted that when camphene from *iso*borneol is oxidised with an alkaline solution of potassium permanganate, the chief product is the isomeride of camphoric acid, known as camphenecamphoric acid, and that some of this acid is also produced when nitric acid is used as the oxidising agent. It is known that camphenecamphoric acid is not an oxidation product of camphene glycol or of camphylic acid, but it has not yet been demonstrated that its constitution is different from that of camphoric acid. If it prove to be the case that these acids are differently constituted, and if at the same time it is assumed that camphenecamphoric acid has the same nucleus as camphene, the formation of this acid cannot be understood if either the formula given above (III) or Wagner's formula for camphene be adopted. The same difficulty arises in connexion with the acid, $C_{10}H_{16}O_2$, obtained by Henderson and Sutherland on oxidising camphene with hydrogen peroxide. There is no evidence, however, that the nuclei of camphene and of camphenecamphoric acid are identical. On the other hand, it is not at all improbable that camphene may undergo molecular rearrangement to some extent under the influence of such reagents as an alkaline



solution of potassium permanganate or hot nitric acid, and this appears to us a probable explanation.

The constitution of *iso*borneol is still uncertain, but it appears to be definitely proved that methylcamphenilol (X), the alcohol which is obtained from camphenilone by means of magnesium methyl iodide, is different from *iso*borneol. For the latter we suggest the formula below (XI), for if this is its constitution it is not difficult to understand the conversion of *iso*borneol into camphene, bornylene, borneol, or camphor respectively; at any rate, the rearrangement which would accompany such changes would be



much less profound than that which would be involved if camphene had the constitution represented by any of the other proposed formulæ.

CHEMISTRY DEPARTMENT,
THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

CCXV.—*The Action of Chlorine on Alkalis and of Carbon Dioxide on Bleaching Powder.*

By ROBERT LLEWELLYN TAYLOR.

IN a former paper (Trans., 1910, **97**, 2541) I stated my conclusions that the action of chlorine on alkalis, like that of bromine and of iodine, is a reversible one, and that the action of carbon dioxide on bleaching powder and similar substances is like that of other acids, the carbonic acid decomposing both the hypochlorite and the chloride.

These conclusions are controverted by S. H. Higgins (this vol., p. 858), and it appears to be necessary to reply to some of his criticisms.

I had pointed out that if the action of chlorine on alkalis is a reversible one, the action would be reversed either (*a*) by the removal of free alkali, or (*b*) by the addition of chlorides to the solution. I showed by actually sweeping it out from the solution that free chlorine is developed in a solution of bleaching powder (*a*) by the removal of free lime, or (*b*) by the addition of chlorides; in the latter case, however, to only a slight extent unless some of the free lime is removed first. I further pointed out that the development of free chlorine naturally stimulates the bleaching action of the solution, and described experiments showing that the bleaching action of a solution of bleaching powder or of sodium hypochlorite is much more rapid after the removal of free alkali, or on the addition of common salt or calcium chloride, provided there is not too much free alkali present.

Higgins says (1) that it is not so much the removal of the free lime from the solution as the further action of the carbon dioxide of the air on the solution after the free lime has been removed that increases the bleaching efficiency; (2) that the action of common salt and of calcium chloride in increasing the bleaching efficiency is due "to the increased attraction of the carbon dioxide of the air by the salt solution"; (3) that other neutral salts of sodium have an effect similar to that of the chloride in stimulating the bleaching action when used in equivalent amounts.

With regard to (1) and (2) it is sufficient to point out that, in the great majority of the author's experiments, after the removal of free alkali or the addition of salt or calcium chloride to the solution, air had no access to the solution; or, when air was used, for example, for sweeping out the chlorine and hypochlorous acid in the solution, the carbon dioxide was removed from it first. Also, in the case of further experiments presently to be described, all of them were performed in closed vessels, to which air had no access. With regard to Higgins' statement (3) that "other neutral salts of sodium have an effect similar to that of the chloride in stimulating the bleaching action," it was considered desirable that further experiments should be made.

Sodium hypochlorite solution was prepared in three different ways: (1) by passing chlorine into a cold solution of sodium hydroxide, (2) by precipitating an aqueous solution of bleaching powder with a normal solution of sodium carbonate, so that the filtered liquid gave no precipitate with either of the solutions, and (3) by exposing a solution of bleaching powder to air in a shallow dish for a few hours, in order to remove some of the free lime, and then precipitating as in (2).

In preparing the hypochlorite by method (1), if the chlorine is passed in too long the solution smells of free chlorine, and bleaches very rapidly, and it is desirable to add more of the alkali. This was usually done until the odour of free chlorine had disappeared, and then the solution was diluted with water until it was of such a strength as to take a reasonable time for each experiment in bleaching.

The rate of bleaching was simply the time required, in comparative experiments, to more or less completely discharge the colour of similar small pieces of Turkey-red calico, previously wetted, and then immersed in the solutions.

The various solutions of hypochlorite were tried (*a*) alone, and (*b*) mixed with varying equivalent amounts of sodium chloride, sodium sulphate, and sodium nitrate. In some experiments the salts were weighed out and added in the solid state to the solutions, but more frequently measured quantities of standard solutions were used, containing respectively 117 grams of common salt, 322 grams of crystallised sodium sulphate, and 168 grams of sodium nitrate per litre.* In all such experiments the bleaching solution with which comparison was being made was diluted with water in volume equal to the amounts of the standard solutions used.

The results of a great number of experiments may be summarised as follows:

* These solutions are $2N$.

I.—If the solution of the hypochlorite contains a considerable excess of free alkali, its bleaching action is extremely slow. In some experiments, when the excess of free alkali was considerable, very little bleaching occurred, even after several days. In such solutions the rate of bleaching is almost unaffected by the addition of any of the salts above mentioned. When any appreciable effect does occur, there is very little difference in the effects of the different salts used. If anything, the sodium chloride has a rather greater effect than either the sulphate or the nitrate.

II.—With solutions of hypochlorite prepared by method (1) (see above), in which only just sufficient alkali was present to prevent the odour of free chlorine in the solution, many different experiments showed that sodium chloride accelerates the bleaching action very considerably, while sodium sulphate and sodium nitrate have little or no action. In some experiments, indeed, the sodium sulphate appeared to have a distinctly retarding effect on the bleaching. The following are two experiments out of many that were tried:

A. Five c.c. of the solution of sodium hypochlorite were used in each case. This was mixed with 5 c.c. of (*a*) water, (*b*) $2N$-solution of sodium chloride, (*c*) $2N$-solution of sodium sulphate, (*d*) $2N$-solution of sodium nitrate. In (*b*) the Turkey-red calico was completely bleached in twenty-two minutes, whilst (*a*), (*c*), and (*d*) all took thirty-five minutes.

B. Same as above, but with a different solution of hypochlorite. In (*a*) the calico was bleached in thirty minutes, in (*b*) twenty minutes, in (*c*) forty minutes, and in (*d*) thirty minutes.

III.—Sodium hypochlorite prepared by method (2) (see above), seeing that solutions of bleaching powder are always strongly alkaline, naturally will also contain a considerable amount of free alkali. The solution therefore bleaches very slowly; but if it has been very carefully prepared, so that there is no excess of sodium carbonate, it practically behaves like the solution prepared by method I; its bleaching action is distinctly accelerated by the addition of sodium chloride, while sodium sulphate and nitrate have little or no effect. If, however, in preparing the solution, any considerable excess of sodium carbonate is used, this has almost the same effect as free alkali. The bleaching action is greatly retarded, and none of the sodium salts has any considerable effect in accelerating it.

IV.—The solution of sodium hypochlorite prepared by method (3) behaves in almost exactly the same way as that prepared by method (1); its bleaching action is greatly accelerated by sodium

chloride, and hardly at all by equivalent amounts of sodium sulphate and nitrate.

As already pointed out (p. 1907), all the above experiments were performed in closed vessels, so that air (other than the small amount which was already in the vessels) had no access; therefore the acceleration of the bleaching action could not have been due to carbon dioxide, as suggested by Higgins.

These additional experiments amply confirm my view as to the reversibility of the action of chlorine on alkalis.

The Action of Carbon Dioxide on Bleaching Powder.

Higgins (*loc. cit.*) also objects to my suggestion that the action of carbonic acid on bleaching powder is the same as that of other acids, the carbonic acid decomposing both the hypochlorite and the chloride. This view would be represented by the following equations:

(1) $Ca(OCl)_2 + H_2O + CO_2 = CaCO_3 + 2HOCl$.

(2) $CaCl_2 + H_2O + CO_2 = CaCO_3 + 2HCl$.

(3) $2HOCl + 2HCl = 2H_2O + 2Cl_2$.

Instead of this, Higgins suggests that the action may be represented thus:

(1) $Ca(OCl)_2 + H_2O + CO_2 = CaCO_3 + 2HOCl$.

(2) $2HOCl + CaCl_2 + CO_2 = CaCO_3 + H_2O + 2Cl_2$.

On comparing these it is obvious that there is really very little difference between them. Higgins' equation (2) is simply a combination of my (2) and (3).

Higgins' equation (2) represents what is no doubt a complex action, and dividing it into two, as I suggest, simplifies it very considerably. As Higgins points out, the reaction is the reverse of Williamson's reaction for the effect of chlorine on water containing calcium carbonate in suspension:

$$CaCO_3 + 2Cl_2 + H_2O = 2HOCl + CaCl_2 + CO_2.$$

This also is a complex action, and doubtless takes place in two steps, the first being the action of chlorine on water (a reversible action), and the second the decomposition of calcium carbonate by hydrochloric acid:

(1) $2H_2O + 2Cl_2 \quad\quad 2HOCl + 2HCl$.

(2) $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$.

I remember quite well that Williamson, in the 'sixties and 'seventies of last century, taught, in his lectures, that chlorine acts on water in the way represented above. He did not say in so many

words that the action was a reversible one, but he probably had such a thing in his mind. He stated in his "Chemistry for Students," of which the last edition was published in 1873, that a solution of chlorine in water always contains both hypochlorous acid and hydrochloric acid, and that the presence of the latter was proved by the fact that silver chloride was precipitated from it when silver nitrate was added. There is hardly any doubt that Williamson would have offered the same explanation of the action of chlorine on water and calcium carbonate as the one suggested above.

MUNICIPAL SCHOOL OF TECHNOLOGY,
MANCHESTER.

CCXVI.—*Experiments on the Walden Inversion. Part VII. Action of Phosphorus Pentachloride and of Thionyl Chloride on Optically Active Hydroxy-acids and Esters.*

By ALEX. McKENZIE and FRED BARROW.

THE comparison of the behaviour of phosphorus pentachloride and of thionyl chloride towards the optically active α-hydroxy-α-phenylpropionic acids, which has been recently described by McKenzie and Clough (Trans., 1910, **97**, 2564), presents a novel aspect of the Walden inversion, inasmuch as, from the *l*-hydroxy-acid, for example, it is possible to obtain either a *d*- or *l*-chloro-acid, thus:

$$l\text{-}{}^{\mathrm{Ph}}_{\mathrm{Me}}\!>\!\mathrm{C}\!<\!{}^{\mathrm{OH}}_{\mathrm{CO_2H}} \xrightarrow{\text{(by } \mathrm{PCl_5}\text{)}} d\text{-}{}^{\mathrm{Ph}}_{\mathrm{Me}}\!>\!\mathrm{C}\!<\!{}^{\mathrm{Cl}}_{\mathrm{CO_2H}}$$

$$l\text{-}{}^{\mathrm{Ph}}_{\mathrm{Me}}\!>\!\mathrm{C}\!<\!{}^{\mathrm{OH}}_{\mathrm{CO_2H}} \xrightarrow[\text{(by } \mathrm{SOCl_2}\text{)}]{} l\text{-}{}^{\mathrm{Ph}}_{\mathrm{Me}}\!>\!\mathrm{C}\!<\!{}^{\mathrm{Cl}}_{\mathrm{CO_2H}}$$

This is obviously an instance where either phosphorus pentachloride or thionyl chloride behaves abnormally, and it is interesting to note that the displacement of the hydroxy-group by the chlorine atom proceeds in a manner parallel with the above when the active ethyl esters are used, thus:

$$l\text{-}{}^{\mathrm{Ph}}_{\mathrm{Me}}\!>\!\mathrm{C}\!<\!{}^{\mathrm{OH}}_{\mathrm{CO_2Et}} \xrightarrow{\text{(by } \mathrm{PCl_5}\text{)}} d\text{-}{}^{\mathrm{Ph}}_{\mathrm{Me}}\!>\!\mathrm{C}\!<\!{}^{\mathrm{Cl}}_{\mathrm{CO_2Et}}$$

$$l\text{-}{}^{\mathrm{Ph}}_{\mathrm{Me}}\!>\!\mathrm{C}\!<\!{}^{\mathrm{OH}}_{\mathrm{CO_2Et}} \xrightarrow[\text{(by } \mathrm{SOCl_2}\text{)}]{} l\text{-}{}^{\mathrm{Ph}}_{\mathrm{Me}}\!>\!\mathrm{C}\!<\!{}^{\mathrm{Cl}}_{\mathrm{CO_2Et}}$$

In the present paper an account is given of the action of phosphorus pentachloride and of thionyl chloride on a number of hydroxy-acids and esters. It is now established that a Walden inversion can be brought about in certain cases with esters of hydroxy-acids, and that the presence of a carboxyl group is not, therefore, a necessary condition for the occurrence of a Walden inversion.

The action of phosphorus pentachloride on *l*-mandelic acid is accompanied by much racemisation (McKenzie and Clough, Trans., 1908, **93**, 811), and the phenylchloroacetic acid formed possesses a dextrorotation which falls considerably below the maximum value. A change of sign of rotation also occurs, as Walden has shown (*Ber.*, 1895, **28**, 1287), when esters of *l*-mandelic acid are acted on by phosphorus pentachloride. The following changes have, accordingly, been already noted:

$$l\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H \xrightarrow{\text{(by } PCl_5)} d\text{-}C_6H_5\cdot CHCl\cdot CO_2H,$$

and

$$l\text{-}C_6H_5\cdot CH(OH)\cdot CO_2Et \xrightarrow{\text{(by } PCl_5)} d\text{-}C_6H_5\cdot CHCl\cdot CO_2Et.$$

We now find that the action of thionyl chloride is different from that of phosphorus pentachloride, inasmuch as the following changes have been effected:

$$l\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H \xrightarrow{\text{(by } SOCl_2)} l\text{-}C_6H_5\cdot CHCl\cdot CO_2H,$$

and

$$l\text{-}C_6H_5\cdot CH(OH)\cdot CO_2Et \xrightarrow{\text{(by } SOCl_2)} l\text{-}C_6H_5\cdot CHCl\cdot CO_2Et.$$

Now, since it has been shown (Trans., 1908, **93**, 811) that *l*-phenylchloroacetic acid can be converted into *d*-mandelic acid by the action of water and silver carbonate, the interconversion of the active mandelic acids can be brought about according to the cycle:

$$\begin{tikzcd}
l\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H \arrow[r, "\text{(by } SOCl_2)"] & l\text{-}C_6H_5\cdot CHCl\cdot CO_2H \arrow[d, "\text{(by } Ag_2CO_3 \text{ and water)}"] \\
d\text{-}C_6H_5\cdot CHCl\cdot CO_2H \arrow[u, "\text{(by } Ag_2CO_3 \text{ and water)}"] & d\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H \arrow[l, "\text{(by } SOCl_2)"]
\end{tikzcd},$$

which may be contrasted with the changes described previously, namely:

$$\begin{tikzcd}
l\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H \arrow[r, "\text{(by } PCl_5)"] & d\text{-}C_6H_5\cdot CHCl\cdot CO_2H \arrow[d, "\text{(by NaOH)}"] \\
l\text{-}C_6H_5\cdot CHCl\cdot CO_2H \arrow[u, "\text{(by NaOH)}"] & d\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H \arrow[l, "\text{(by } PCl_5)"]
\end{tikzcd}.$$

The racemisation which accompanies the displacement of the

hydroxy-group by the chlorine atom is much less pronounced when thionyl chloride is used in place of phosphorus pentachloride. In the case of the acid this is probably due to some extent to the fact that the action of thionyl chloride can be conducted at comparatively low temperatures. The phenylchloroacetic acid obtained by the interaction of thionyl chloride and *l*-mandelic acid had $[\alpha]_D$ $-101\cdot3°$ in benzene solution, whereas the pure acid, free from the *r*-isomeride, has $[\alpha]_D$ $-191°$ in the same solvent. Again the dextrorotatory ethyl phenylchloroacetate, prepared by Walden (*loc. cit.*) by the action of phosphorus pentachloride on a solution of ethyl *l*-mandelate in chloroform, had $[\alpha]_D$ $+25\cdot19°$, whilst the product obtained by the authors from thionyl chloride and ethyl *l*-mandelate possesses a much higher activity, namely, $[\alpha]_D$ $-64°$. A Walden inversion occurs, of course, in the case of the ester, either with phosphorus pentachloride or with thionyl chloride, but, although the racemisation is pronounced in the former case, this aspect can hardly be emphasised in favour of the view that phosphorus pentachloride acts abnormally.

The action of thionyl chloride on *r*-mandelic acid has been studied by Hans Meyer (*Monatsh.*, 1901, **22**, 415), who states: "Mandelsäure wird glatt unter Bildung von Benzaldehyd gespalten," and the formation of benzaldehyde is assumed to occur, owing to the disruption of the sulphito-chloride, $C_6H_5\cdot CH(OSOCl)\cdot COCl$, with evolution of carbon monoxide and regeneration of thionyl chloride. We were unable to confirm this observation. Phenylchloroacetic acid is produced, although in small yield, by the action of water on the oil resulting from the treatment of *r*-mandelic acid with thionyl chloride, whilst the main product is benzylidene chloride. There was no evidence of the presence of benzaldehyde, and the action probably occurs according to the equations:

$$(1)\quad C_6H_5\cdot CH(OH)\cdot CO_2H + 2SOCl_2 = C_6H_5\cdot CH(O\cdot SOCl)\cdot COCl + 2HCl + SO_2.$$

$$(2)\quad C_6H_5\cdot CH(O\cdot SOCl)\cdot COCl = C_6H_5\cdot CHCl_2 + SO_2 + CO.$$

$$(3)\quad C_6H_5\cdot CH(O\cdot SOCl)\cdot COCl = C_6H_5\cdot CHCl\cdot COCl + SO_2.$$

It is, however, conceivable that benzaldehyde is actually formed as an intermediate product, more especially since Hoering and Baum (*Ber.*, 1908, **41**, 1918) mention that benzylidene chloride can be formed in almost quantitative yield by the interaction of thionyl chloride and benzaldehyde.

As is well known, the action of phosphorus pentachloride on *l*-malic acid (or its esters) is accompanied by a change of sign of rotation (Walden). The authors have examined the behaviour of

thionyl chloride, and find that it is similar to that of pentachloride, thus:

$$l\text{-}\begin{array}{l}CH(OH)\cdot CO_2H\\ |\\ CH_2\cdot CO_2H\end{array} \xrightarrow{\text{(by } SOCl_2)} d\text{-}\begin{array}{l}CHCl\cdot CO_2H\\ |\\ CH_2\cdot CO_2H\end{array}$$

and

$$l\text{-}\begin{array}{l}CH(OH)\cdot CO_2Et\\ |\\ CH_2\cdot CO_2Et\end{array} \xrightarrow{\text{(by } SOCl_2)} d\text{-}\begin{array}{l}CHCl\cdot CO_2Et\\ |\\ CH_2\cdot CO_2Et\end{array}.$$

The sulphito-ester, obtained from thionyl chloride and ethyl *d*-tartrate, was found to possess a much higher lævorotation than that quoted by Schiller (*Ber.*, 1909, **42**, 2017). Attempts to bring about the interconversion of the optically active tartaric acids by the aid of this compound were unsuccessful.

McKenzie and Wren (Trans., 1910, **97**, 1355) have already described the interconversion of the optically active *α*-hydroxy-*β*-phenylpropionic acids which has been effected according to the cycle:

$$\begin{tikzcd}
d\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H \arrow[r, dashed, "\text{(by } PCl_5)"] & l\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot CO_2H \arrow[d, "\text{(by } CaCO_3 \text{ and water)}"] \\
d\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot CO_2H \arrow[u, "\text{(by } CaCO_3 \text{ and water)}"] & l\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H \arrow[l, "\text{(by } PCl_5)"']
\end{tikzcd}$$

The oil obtained by the action of phosphorus pentachloride on the *d*-hydroxy-acid was dextrorotatory, but since it gave the *l*-hydroxy-acid on decomposition with calcium carbonate and water, it is probable that *d*-*α*-chloro-*β*-phenylpropionyl chloride corresponds in configuration with *l*-*α*-chloro-*β*-phenylpropionic acid. It was shown that the displacement of bromine in the active *α*-bromo-*β*-phenylpropionic acids gave hydroxy-acids of the same sign of activity as the bromo-acid used, no matter under what conditions the displacement was conducted; this action may be taken as normal. Further, it was pointed out that the action of phosphorus pentachloride is doubtless abnormal, the assumption being made that the behaviour of the active *α*-chloro-*β*-phenylpropionic acids towards calcium carbonate and water is similar to that of the *α*-bromo-*β*-phenylpropionic acids.

We have carried out a considerable number of experiments on the behaviour of the active ethyl esters of *α*-hydroxy-*β*-phenylpropionic acid towards phosphorus pentachloride and thionyl chloride respectively, and also on the action of thionyl chloride on the free acids. These changes are unfortunately complicated by the occurrence of side-reactions (compare Scheibler and Wheeler, *Ber.*, 1911, **44**, 2689), and our results have on this account little value. It is well known from the work of Anschütz and others that the action of phosphorus pentachloride on hydroxy-compounds

is frequently attended with the formation of phosphorus derivatives, whilst Bistrzycki and Landtwing (*Ber.*, 1908, **41**, 686), in continuation of the exhaustive researches of the former on carbon monoxide scission, have shown how readily the latter phenomenon occurs when certain acid chlorides are heated. It appears, however, that phosphorus pentachloride and thionyl chloride behave differently towards the active esters, inasmuch as the direction of rotation is unchanged with the former, and changed with the latter. The action of phosphorus pentachloride may accordingly be used to interconvert the acids as follows:

$$\begin{array}{ccc} l\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H & \xrightarrow{\text{(by HCl and EtOH)}} & l\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2Et \\ & & \downarrow \text{(by PCl}_5\text{)} \\ d\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H & \xleftarrow[\text{(by CaCO}_3\text{ and aqueous EtOH)}]{} & l\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot CO_2Et \end{array}$$

Inasmuch as we find that the lævorotatory acid chloride resulting from the interaction of phosphorus pentachloride and the *l*-hydroxy-acid gives a lævorotatory ester when acted on by ethyl alcohol, it is possible that the acids can be interconverted according to the following changes:

$$l\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H \longrightarrow l\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot COCl \longrightarrow$$
$$l\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot CO_2Et \longrightarrow d\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H.$$

The contrast with thionyl chloride is indicated by the following scheme:

$$\begin{array}{ccc} l\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H & \xrightarrow{\text{(by HCl and EtOH)}} & l\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2Et. \\ & & \downarrow \text{(by SOCl}_2\text{)} \\ & \nwarrow \text{(by CaCO}_3\text{ and aqueous EtOH)} & d\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot CO_2Et \end{array}$$

Since the bulk of the research on the Walden inversion has been confined to α-hydroxy-acids and their derivatives, the investigation of β-hydroxy-acids, where the carboxyl group is not directly attached to the asymmetric carbon atom, is of particular importance. At first it appeared that a Walden inversion could not be effected with this type, for example:

$$(1)\ l\text{-}CH_3\cdot CH(OH)\cdot CH_2\cdot CO_2H \underset{\text{(by Ag}_2\text{O or water)}}{\overset{\text{(by PCl}_5\text{)}}{\rightleftarrows}} d\text{-}CH_3\cdot CHCl\cdot CH_2\cdot CO_2H$$

(E. Fischer and Scheibler, *Ber.*, 1909, **42**, 1219.)

$$(2)\ l\text{-}C_6H_5\cdot CH(OH)\cdot CH_2\cdot CO_2H \underset{\text{(by Ag}_2\text{O or water or Na}_2\text{CO}_3\text{)}}{\overset{\text{(by HBr or PBr}_5\text{)}}{\rightleftarrows}} d\text{-}C_6H_5\cdot CHBr\cdot CH_2\cdot CO_2H$$

(McKenzie and Humphries, Trans., 1910, **97**, 121.)

$$(3)\quad d\text{-}C_6H_5\cdot CH(NH_2)\cdot CH_2\cdot CO_2H \xrightarrow{\text{(by } HNO_2\text{)}} l\text{-}C_6H_5\cdot CH(OH)\cdot CH_2\cdot CO_2H$$
$$d\text{-}C_6H_5\cdot CH(NH_2)\cdot CH_2\cdot CO_2Et \xrightarrow{\text{(by } HNO_2\text{)}} l\text{-}C_6H_5\cdot CH(OH)\cdot CH_2\cdot CO_3Et$$

(E. Fischer, Scheibler, and Groh, *Ber.*, 1910, **43**, 2020.)

It has, however, been recently shown by E. Fischer and Scheibler (*Sitzungsber. K. Akad. Wiss. Berlin*, 1911, **26**, 566; *Annalen*, 1911, **383**, 337) that the following changes can be carried out:

$$\begin{array}{ccc} d\text{-}CH_3\cdot CH(NH_2)\cdot CH_2\cdot CO_2H & \xrightarrow{\text{(by } HNO_2\text{)}} & l\text{-}CH_3\cdot CH(OH)\cdot CH_2\cdot CO_2H \\ \downarrow{\scriptstyle\text{(by NOCl)}} & & \\ l\text{-}CH_3\cdot CHCl\cdot CH_2\cdot CO_2H & \xrightarrow{\text{(by water)}} & d\text{-}CH_3\cdot CH(OH)\cdot CH_2\cdot CO_2H \end{array}$$

It is therefore obvious that a Walden inversion must have occurred during one of these stages, and the phenomenon is accordingly not confined to α-substituted acids.

In this connexion we have studied the optically active β-hydroxy-β-phenylpropionic acids. The action of hydrochloric acid and of phosphorus pentachloride on the d-hydroxy-acid gives a lævorotatory chloro-acid, and when this is boiled with water the parent hydroxy-acid is regenerated (compare McKenzie and Humphries, *loc. cit.*), thus:

$$d\text{-}C_6H_5\cdot CH(OH)\cdot CH_2\cdot CO_2H \underset{\text{(by water)}}{\overset{\text{(by HCl or } PCl_5\text{)}}{\rightleftarrows}} l\text{-}C_6H_5\cdot CHCl\cdot CH_2\cdot CO_2H$$

The behaviour of thionyl chloride is, however, different, and the interconversion of the hydroxy-acids was realised in accordance with the following scheme:

$$\begin{array}{ccc} d\text{-}C_6H_5\cdot CH(OH)\cdot CH_2\cdot CO_2H & \xrightarrow{\text{(by } SOCl_2\text{)}} & d\text{-}C_6H_5\cdot CHCl\cdot CH_2\cdot CO_2H \\ \uparrow{\scriptstyle\text{(by water)}} & & \downarrow{\scriptstyle\text{(by water)}} \\ l\text{-}C_6H_5\cdot CHCl\cdot CH_2\cdot CO_2H & \xleftarrow[\text{(by } SOCl_2\text{)}]{} & l\text{-}C_6H_5\cdot CH(OH)\cdot CH_2\cdot CO_2H \end{array}$$

These changes are accompanied with a considerable amount of racemisation. It was noteworthy that the action of thionyl chloride gave a much more active acid chloride than in the case of phosphorus pentachloride; with thionyl chloride the crude product resulting from the d-hydroxy-acid had $\alpha_D^{17\cdot5} + 25\cdot38°$ in a 50 mm. tube, whilst with pentachloride α_D was only $-1\cdot25°$. The former product was necessarily contaminated with cinnamoyl chloride owing to the elimination of hydrogen chloride during the preparation; when, however, it was decomposed by water, the cinnamic and the hydroxy-acid were easily separated from one another. We consider it probable that the Walden inversion is caused by the thionyl chloride, and not by the water.

The above-mentioned cycle represents the first instance recorded of the interconversion of β-hydroxy-acids by the Walden inversion.

Experimental.

Action of Thionyl Chloride on r-*Mandelic Acid.*

Fifty grams of *r*-mandelic acid were heated with 100 grams of thionyl chloride for seven hours until the evolution of hydrogen chloride ceased. After removal of the excess of thionyl chloride, 30 grams of a pale yellow oil, boiling at 90—120°/13 mm., were collected, and then the product in the distilling flask began to decompose. Since the oil had not solidified when left overnight in contact with a large excess of water, it was separated from the latter by means of ether, and the acid present in the ethereal solution was removed by aqueous sodium carbonate. The phenylchloroacetic acid obtained from the sodium salt by acidification with mineral acid and extraction with ether amounted to 7·5 grams. The ethereal solution from which the phenylchloroacetic acid had been removed was evaporated, and the residual oil fractionated under diminished pressure, when it was found to consist mainly of benzylidene chloride. The latter compound was isolated without difficulty, and identified by its odour, boiling point, and analysis.

Action of Thionyl Chloride on l-*Mandelic Acid. Conversion of* l- *into* d-*Mandelic Acid.*

Ten grams of *l*-mandelic acid (1 mol.) and 24 grams of thionyl chloride (3 mols.) were heated at 50° for one hour, then boiled gently during two hours, and finally allowed to remain at the ordinary temperature for seven days. After removal of the thionyl chloride, the residual yellow oil was distilled under diminished pressure, when 4·5 grams, boiling at 97—102°/13 mm., were collected. This oil showed no tendency to solidify when left in contact with water overnight, whereas the product obtained by the interaction of phosphorus pentachloride and *l*-mandelic acid (Trans., 1908, **93**, 811) readily solidifies under these conditions. The phenylchloroacetic acid which was isolated as indicated in the preceding experiment amounted to 2·1 grams. It melted at 45—52° to a turbid liquid, which became clear at 65°, and was a mixture of the *r*- and *l*-acids, with the following rotation in benzene solution:

$$l=2,\ c=3\cdot656,\ \alpha_D^{16}\ -7\cdot41°,\ [\alpha]_D^{16}\ -101\cdot3°.$$

On crystallising this acid from a mixture of benzene and light petroleum, the crystals which separated contained a larger proportion of the racemic acid than did the original acid (compare Trans., 1909, **95**, 785), the following value for the specific rotation having been determined in benzene solution:

$$l=2,\ c=1\cdot702,\ \alpha_D^{14}\ -1\cdot49°,\ [\alpha]_D^{14}\ -43\cdot8°.$$

The mother liquor from this product was allowed to evaporate spontaneously at the ordinary temperature. The resulting phenylchloroacetic acid (1·05 grams) had, of course, a higher optical activity than that of the original acid. In benzene solution:

$$l=2,\ c=2\cdot394,\ \alpha_D^{14}\ -7\cdot00°,\ [\alpha]_D^{14}\ -146\cdot2°.$$

0·1265, dissolved in ethyl alcohol, required 23·5 c.c. $N/31\cdot5$-baryta for neutralisation, the calculated amount being 23·4 c.c.

The pure *l*-acid obtained by the resolution of the *r*-acid with morphine (*loc. cit.*) has $[\alpha]_D^{12}$ $-191°$ in benzene solution.

When the chlorine in the above lævorotatory acid was displaced by the hydroxy-group by the aid of silver carbonate and water, a dextrorotatory mandelic acid was obtained. The chloro-acid (0·65 gram) with $[\alpha]_D$ $-146\cdot2°$ was shaken with 40 c.c. of water at the ordinary temperature for half a minute, and then treated with silver carbonate, which had been freshly precipitated from 2 grams of nitrate. After one and a-half hours at the ordinary temperature with occasional shaking, the mixture was heated on the water-bath for one and a-half hours. Dilute hydrochloric acid was added, and the silver chloride removed. The filtrate (60 c.c.) was dextrorotatory, 25 c.c. of it in a 4-dcm. tube giving α_D $+1\cdot39°$. The mandelic acid extracted from this solution in the usual manner gave the following value in ethyl-alcoholic solution:

$$l=2,\ c=1\cdot73,\ \alpha_D^{13}\ +1\cdot83°,\ [\alpha]_D^{13}\ +52\cdot9°.$$

Action of Thionyl Chloride on l-*Mandelic Esters.*

Methyl *l*-mandelate (4·3 grams) and thionyl chloride (12 grams) were mixed, and allowed to remain at the ordinary temperature for twenty-four hours. Since the action was incomplete, the solution was heated at 50—60° for one hour, and finally on the water-bath for two hours until the evolution of hydrogen chloride ceased. The ester was then distilled under diminished pressure, when 3·8 grams were obtained.

Methyl l-*phenylchloroacetate*, $C_6H_5\cdot CHCl\cdot CO_2Me$, is a colourless oil, boiling at 123—126°/11 mm.:

0·251 gave 0·1956 AgCl. Cl = 19·3.

$C_9H_9O_2Cl$ requires Cl = 19·2 per cent.

The specific rotation was determined:

$$l=1,\ D_4^{15}\ 1\cdot213,\ \alpha_D^{15}\ -105\cdot15°,\ [\alpha]_D^{15}\ -86\cdot7°.$$

The hydrolysis of this ester was conducted as follows. One gram was added to 10 c.c. of aqueous hydrochloric acid saturated at 0°, and the mixture kept at the ordinary temperature for six days, with occasional shaking. When the viscid oil was nucleated with *l*-phenylchloroacetic acid, crystals began to form slowly after a time.

Water was added, and the mixture of acid and unattacked ester extracted with ether. The acid was removed from the ethereal solution by aqueous sodium carbonate, and was then isolated in the usual manner. The resulting phenylchloroacetic acid (0·42 gram) was lævorotatory in benzene solution:

$$l=2,\ c=2{\cdot}09,\ \alpha_D\ -3{\cdot}27°,\ [\alpha]_D\ -78{\cdot}2°.$$

0·1078, in ethyl-alcoholic solution, required 19·8 c.c. $N/31{\cdot}5$-baryta for neutralisation. Calc., 19·9 c.c.

Ethyl *l*-mandelate (7 grams) and thionyl chloride (20 grams) were mixed, and kept at the ordinary temperature for four days, by which time the evolution of hydrogen chloride had ceased. *Ethyl* l-*phenylchloroacetate* is a colourless oil, and boils at 132—133°/15 mm.:

0·3366 gave 0·2406 AgCl. Cl=17·7.

$C_{10}H_{11}O_2Cl$ requires Cl=17·9 per cent.

The specific rotation was determined:

$$l=0{\cdot}5,\ D_4^{16\cdot4}\ 1{\cdot}162,\ \alpha_D^{16\cdot4}\ -37{\cdot}18°,\ [\alpha]_D^{16\cdot4}\ -64{\cdot}0°.$$

The phenylchloroacetic acid obtained by conducting the hydrolysis in the manner already described in the case of the methyl ester was lævorotatory in benzene solution:

$$l=2,\ c=3{\cdot}26,\ \alpha_D\ -4{\cdot}38°,\ [\alpha]_D\ -67{\cdot}2°.$$

The displacement of chlorine in methyl *l*-phenylchloroacetate by alkyloxy-groups was examined. A solution of 1 gram of the chloro-ester in 10 c.c. of methyl alcohol was boiled for one and a-half hours with a solution of 0·4 gram of sodium in 5 c.c. of methyl alcohol. The sodium chloride was drained off, and the filtrate, when polarimetrically examined in a 2-dcm. tube, was found to be inactive. The acid isolated from the sodium salt was identified by its melting point and analysis as *r*-phenylmethoxyacetic acid.

The behaviour of sodium ethoxide towards the chloro-ester was similar.

This type of racemisation has a parallel in the observations of Purdie and Williamson (Trans., 1896, **69**, 820) dealing with the action of sodium ethoxide on ethyl *d*-α-chloropropionate and ethyl *l*-α-bromopropionate respectively. It was suggested by these authors that in actions of this type, halogen acid is eliminated with the subsequent addition of alcohol, a view which has support from the behaviour of esters of unsaturated acids towards alcohols in the presence of traces of sodium ethoxide.

Action of Thionyl Chloride on l-*Malic Acid.*

Eight grams of powdered *l*-malic acid and 28 grams of thionyl chlorides were allowed to remain at the ordinary temperature, when

a slow evolution of hydrogen chloride took place. After nine days the solid present was removed, and found by analysis and determination of rotation to consist of unaltered malic acid.

The displacement, however, of the alcoholic hydroxy-group in malic acid takes place readily under the following conditions. Six grams of the acid and 22 grams of thionyl chloride were heated on the water-bath for one hour. The action was vigorous, and the acid gradually dissolved. The excess of thionyl chloride was removed under diminished pressure, and the residual viscid oil was dissolved in 50 c.c. of water. The chlorosuccinic acid was separated from the malic acid present by extraction with ether. The yield of crude chloro-acid was 2 grams, and, after one crystallisation from benzene containing a little acetone, it melted at 174—176°. The specific rotation was determined in aqueous solution:

$$l=2,\ c=2{\cdot}706,\ \alpha_D^{18\cdot5}\ +1{\cdot}09°,\ [\alpha]_D^{18\cdot5}\ +20{\cdot}1°.$$

Tilden and Marshall (Trans., 1895, **67**, 494) give $[\alpha]_D^{19}\ -19{\cdot}67°$ for *l*-chlorosuccinic acid, obtained by the action of nitrosyl chloride on *l*-asparagine. According to Walden (*Zeitsch. physikal. Chem.*, 1895, **17**, 253), *d*-chlorosuccinic acid, obtained by the action of phosphorus pentachloride on *l*-malic acid, melts at 174°, and has $[\alpha]_D\ +20{\cdot}27°$.

It is therefore possible to obtain readily by the above method the pure *d*-chloro-acid by the action of thionyl chloride on *l*-malic acid. Partial racemisation does, however, occur if the initial heating with thionyl chloride is prolonged. For example, when 7 grams of *l*-malic acid were heated with 24 grams of thionyl chloride for three and a-half hours, the crude chlorosuccinic acid amounted to $1\frac{1}{2}$ grams, and even after two crystallisations from benzene containing a little acetone, its melting point was low, namely, 155—159°, and its specific rotation in aqueous solution was only $+14{\cdot}1°$.

Action of Thionyl Chloride on Ethyl l-*Malate.*

Ethyl *l*-malate (7·6 grams, 1 mol.) was added to thionyl chloride (5·5 grams, 1 mol.), and, after four days at the ordinary temperature, the liquid was distilled under diminished pressure. The optical activity of the main fraction was determined, and the value obtained did not alter when the product was redistilled. Yield, 6 grams.

Ethyl d-*chlorosuccinate*, $CO_2Et{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2Et$, is a colourless oil, which boils at 124°/18 mm.:

0·2713 gave 0·1858 AgCl. Cl = 16·9.

$C_8H_{13}O_4Cl$ requires Cl = 17·0 per cent.

It has $D_4^{19\cdot5}$ 1·152 and $\alpha_D^{19\cdot8}\ +37{\cdot}73°\ (l=1)$; whence $[\alpha]_D^{19\cdot8}\ +32{\cdot}7°$.

The latter value is higher than that quoted by Walden (*Ber.*, 1895, **28**, 1290), who prepared the ester from *d*-chlorosuccinic acid by the hydrogen chloride method, and obtained a product with $[\alpha]_D +27\cdot5^\circ$. Walden's ester was thus partly racemised, but it is also doubtful if the compound, as obtained by us, possesses the maximum activity, especially since we find that partial racemisation does actually occur when the temperature is raised during the interaction of thionyl chloride (in slight excess) and ethyl *l*-malate. For example, 10 grams of the malate and 10 grams of thionyl chloride were allowed to remain for fifteen hours at the ordinary temperature, after which time a slight evolution of hydrogen chloride was still perceptible. The action was completed by boiling on the water-bath for three-quarters of an hour. The resulting ester had $\alpha_D^{18} +31\cdot04^\circ$ in a 1-dcm. tube. Further, the ester with $[\alpha]_D^{19\cdot8} +32\cdot7^\circ$ gave a partly racemised chlorosuccinic acid when it was hydrolysed with fuming hydrochloric acid, but, of course, this effect may have been brought about during the hydrolysis; the chloro-acid obtained melted indefinitely at 162—166°, and had $[\alpha]_D +18\cdot7^\circ$ in aqueous solution.

Action of Thionyl Chloride on Ethyl d-*Tartrate.*

Carius (*Annalen*, 1859, **111**, 94) has shown that esters of sulphurous acid are formed by the interaction of thionyl chloride and alcohols, whilst Moers (*Inaug. Diss.*, Berlin, 1907) obtained the compound $(OEt)_2CH\cdot CH{<}{\begin{smallmatrix} CH_2\cdot O \\ O\text{——}SO \end{smallmatrix}}$ by the action of thionyl chloride on glycerol acetal. Schiller (*Ber.*, 1909, **42**, 2017) accordingly studied the behaviour of tartaric esters towards thionyl chloride, and showed that the action proceeds thus:

$$\begin{matrix} CH(OH)\cdot CO_2Et \\ | \\ CH(OH)\cdot CO_2Et \end{matrix} + SOCl_2 = 2HCl + SO{<}\begin{matrix} O\cdot CH\cdot CO_2Et \\ | \\ O\cdot CH\cdot CO_2Et \end{matrix}.$$

Since this sulphito-ester, as described by Schiller, has a rotation opposite in sign to the tartrate used, we were led to prepare it with the object of regenerating tartaric acid from it in order to find out whether an interconversion of the active tartaric acids could be effected through a Walden inversion. Such an interconversion does not, however, occur.

The method employed differed in detail from that described by Schiller, and it gave a satisfactory yield of a product, which, on polarimetric examination, gave a value very much higher than Schiller's. Evolution of hydrogen chloride began at once at the ordinary temperature when 12 grams of thionyl chloride were added to 15 grams of ethyl *d*-tartrate. After two weeks at the ordinary

temperature, the thionyl chloride was removed, and the residue distilled under diminished pressure. A pale yellow oil was obtained boiling at 160°/12 mm., whereas Schiller gives 167°/11·5 mm. (Found, S=12·6. Calc., S=12·7 per cent.)

The following values were obtained:

$$l=1,\ D_4^{19\cdot5}\ 1\cdot329,\ \alpha_D^{19\cdot5}\ -244\cdot3°,\ [\alpha]_D^{19\cdot5}\ -183\cdot8°;$$
$$l=0\cdot5,\ D_4^{9\cdot5}\ 1\cdot342,\ \alpha_D^{9\cdot5}\ -124\cdot4°,\ [\alpha]_D^{9\cdot5}\ -185\cdot4°.$$

Schiller's values are as follows:

$$D^{19\cdot5}\ 1\cdot3257,\ [\alpha]_D^{17\cdot5-18}\ -56\cdot71°.$$

We have also examined the compound in ethyl-alcoholic solution, with the result:

$$l=2,\ c=4\cdot703,\ \alpha_D\ -17\cdot78°,\ [\alpha]_D\ -189\cdot0°.$$

The ester was then decomposed by heating with aqueous sodium hydroxide, when sulphurous acid was readily eliminated. In this operation a change of sign of rotation occurred, and *d*-tartaric acid was obtained from the product by conversion into lead salt and decomposition of the latter with hydrogen sulphide.

Action of Phosphorus Pentachloride on d- *and* l-*α-Hydroxy-β-phenylpropionates.*

d-α-Hydroxy-β-phenylpropionic acid, prepared as previously described (Trans., 1910, **97**, 1355) by the resolution of the *r*-acid by morphine, was converted into its ethyl ester by the hydrogen chloride method.

Ethyl d-*α-hydroxy-β-phenylpropionate*,

$$C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2Et,$$

when freshly distilled, is a colourless oil, and boils at 152—154°/20 mm. It has D_4^{17} 1·105 and α_D^{17} +8·40°; whence α_D^{17} +7·6°.

On keeping overnight, the ester in the neck of the distilling flask used had solidified, and, after some days, a nucleus of this solid was added to the main lot of oil, when solidification of the latter occurred at once. Several preparations both of this ester and of its *l*-isomeride were carried out subsequently, but on no occasion did these esters fail to solidify soon after distillation, and when left exposed to the atmosphere of the laboratory, which had in the meantime doubtless become infected with the esters (compare Biilmann's work on the isomerism of the cinnamic acids).*

The solid *d*-ester melts at 46—47°:

0·2375 gave 0·5923 CO_2 and 0·1574 H_2O. C=68·0; H=7·4.

$C_{11}H_{14}O_3$ requires C=68·0; H=7·3 per cent.

* The corresponding *dl*-ester, prepared from ethyl β-phenyl-α-diazopropionate by Curtius and Müller (*Ber.*, 1904, **37**, 1268), is described as an oil.

The ester separates from light petroleum (b. p. 60—80°) in fine, long, felted needles. It is readily soluble in cold ethyl alcohol, benzene, or acetone, and, when its specific rotation was determined in these solvents, it was found to be lævorotatory in ethyl-alcoholic solution:

$$l=2,\ c=6{\cdot}074,\ \alpha_D^{18\cdot5}\ -0{\cdot}58°,\ [\alpha]_D^{18\cdot5}\ -4{\cdot}8°.$$

In benzene solution:

$$l=2,\ c=3{\cdot}982,\ \alpha_D^{17\cdot5}\ +1{\cdot}79°,\ [\alpha]_D^{17\cdot5}\ +22{\cdot}5°.$$

In acetone solution:

$$l=2,\ c=4{\cdot}272,\ \alpha_D^{17\cdot5}\ +1{\cdot}16°,\ [\alpha]_D^{17\cdot5}\ +13\ 6°.$$

The enantiomorphously related ester was also prepared from the *l*-acid.

Ethyl l-*α-hydroxy-β-phenylpropionate* boils at 159—160°/26 mm., and solidified on cooling. It has m. p. 46—47°, and the value for its rotation in benzene solution was in agreement with that of the *d*-ester:

$$l=2,\ c=4{\cdot}03,\ \alpha_D^{13}\ -1{\cdot}82°,\ [\alpha]_D^{13}\ -22{\cdot}6°.$$

The *l*-hydroxy-ester (6 grams) was heated with phosphorus pentachloride (6·7 grams) for about two hours at 100°, but, judging from the amount of pentachloride which had separated out overnight, it was obvious that the action was incomplete under these conditions. After one hour at 130°, the product was then distilled under diminished pressure, and the fraction boiling between 152° and 170°/18 mm. was collected. It was *laevorotatory*, giving $\alpha_D -2{\cdot}2°$ in a 1-dcm. tube. Attempts to prepare a uniform product from it by further fractionation were unsuccessful. The various fractions, amounting to 5 grams, were then hydrolysed by boiling with calcium carbonate and aqueous alcohol, and a *dextrorotatory* aqueous solution of calcium salt was obtained, the observed value in a 2-dcm. tube being $\alpha_D +0{\cdot}63°$.

The *d*-hydroxy-ester, when treated in chloroform solution with phosphorus pentachloride, gave a similar result.

The *l*-hydroxy-acid (4·7 grams) was acted on by phosphorus pentachloride (11·7 grams), as described by McKenzie and Wren (*loc. cit.*) for the *d*-acid. After distillation under diminished pressure, the product was lævorotatory, its solution in an equal volume of ether giving $\alpha_D -8{\cdot}5°$ in a 1-dcm. tube. On treatment with ethyl alcohol, an oil was obtained; the main portion boiled at 162—171°/23 mm. The amount of material was too small to admit of further purification, but it was found that the liquid gave $[\alpha]_D -12{\cdot}1°$ in ethyl-alcoholic solution.

Action of Thionyl Chloride on Ethyl l-*α-Hydroxy-β-phenylpropionate.*

Ethyl *l*-α-hydroxy-β-phenylpropionate (6 grams) and thionyl chloride (12 grams) were allowed to remain at the ordinary temperature for one and a-half hours, then heated within half an hour to 50°, and maintained at this temperature for one hour, and finally heated for two and a-half hours on the water-bath. On fractionation, 3·5 grams, b. p. 129—138°/8 mm., were obtained, and this was *dextrorotatory*, giving α_D +19·18° in a 50 mm. tube. On decomposition with calcium carbonate and aqueous alcohol, it gave an aqueous solution of calcium salt, which was *laevorotatory*.

Several experiments were also carried out on the action of thionyl chloride on the *r*- and *l*-hydroxy-acids with no positive result, owing to the decomposition which occurred during the distillation of the acid chloride.

Action of Hydrochloric Acid on d- *and* l-*β-Hydroxy-β-phenylpropionic Acids.*

The optically active acids were prepared from the *r*-acid by the method previously described (Trans., 1910, **97**, 121).

Eight grams of *d*-β-hydroxy-β-phenylpropionic acid were added to 120 c.c. of fuming hydrochloric acid (saturated at 0°), cooled to −10°. On shaking, the bulk of the hydroxy-acid dissolved, and, after ten minutes, the chloro-acid began to crystallise out. The mixture remained in the freezing mixture for two hours, and, after fifteen hours at the ordinary temperature, the voluminous precipitate was drained off; yield about 8 grams, $[\alpha]_D$ in ethyl-alcoholic solution −12°. The acid, when crystallised from benzene, separated in lustrous leaflets (6·2 grams) with $[\alpha]_D$ −7·1° in ethyl alcohol. This acid contained 18·85 per cent. Cl, whereas

$$C_6H_5 \cdot CHCl \cdot CH_2 \cdot CO_2H$$

requires 19·2 per cent. After one further crystallisation, the optical activity dropped to $[\alpha]_D$ −4·6° in ethyl alcohol. (Found, Cl = 19·0 per cent.) A change of sign of rotation took place when the chlorine in the latter acid was displaced by the hydroxy-group by boiling with water. A little cinnamic acid was formed in this operation. The resulting hydroxy-acid was slightly but distinctly dextrorotatory; a solution of 3 grams, made up to 20 c.c. of ethyl alcohol, gave α_D +0·29° in a 4-dcm. tube, and the dextrorotation still was evident when the product was crystallised from benzene.

The change

$$l\text{-}C_6H_5 \cdot CHCl \cdot CH_2 \cdot CO_2H \longrightarrow d\text{-}C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CO_2H$$

was also confirmed by the action of water on the chloro-acid, obtained from the mother liquors, from which the acids with $[\alpha]_D -7{\cdot}1°$ and $-4{\cdot}6°$ had been removed. Two grams of this acid with $[\alpha]_D -21{\cdot}7°$ were boiled with water in an open flask for one and a-quarter hours. Some styrene was produced, and also a little cinnamic acid, which was removed. The hydroxy-acid was extracted with ether in a continuous extraction apparatus. It amounted to 1·1 grams, and was dextrorotatory, 0·8658, dissolved in ethyl alcohol and made up to 10 c.c., giving $\alpha_D +0{\cdot}21°$ in a 2-dcm. tube. The dextrorotation persisted in the product obtained by crystallisation from benzene, the $[\alpha]_D$ being only $+0{\cdot}9°$ in ethyl alcohol. (Found, C = 64·9; H = 6·3. Calc., C = 65·0; H = 6·1 per cent.)

The optical activity of the crude chloro-acid varies considerably in value according to the conditions under which the action of hydrochloric acid is conducted. In the preceding experiment, the specific rotation of the crude acid was $-12°$, but in one experiment with the *l*-hydroxy-acid, when the product was removed after four hours at about $-15°$ in contact with fuming hydrochloric acid, the crude chloro-acid had $[\alpha]_D +21{\cdot}8°$. On the other hand, in an experiment with the *l*-hydroxy-acid where the action was conducted at the ordinary temperature, the $[\alpha]_D$ of the product was only $+6{\cdot}5°$.

Action of Phosphorus Pentachloride on d-*β-Hydroxy-β-phenylpropionic Acid.*

Phosphorus pentachloride (21 grams) was gradually added to *d*-*β*-hydroxy-*β*-phenylpropionic acid (8 grams), the operation being conducted by cooling the mixture to $-15°$ from time to time in order to avoid, so far as possible, any racemisation which might occur by the temperature being too high. After five days at the ordinary temperature, a small amount of pentachloride remained unattacked, and the mixture was therefore heated for ten minutes until all dissolved. After removal of the phosphoryl chloride, the residue containing the chloro-chloride was *laevorotatory*, giving $\alpha_D^{17\cdot5} -1{\cdot}25°$ in a 50 mm. tube. This oil was decomposed by moist ether, and the solid product containing the chloro-acid was also lævorotatory in ethyl-alcoholic solution:

$$l = 4,\ c = 8{\cdot}5184,\ \alpha_D -0{\cdot}44°,\ [\alpha]_D -1{\cdot}3°.$$

Action of Thionyl Chloride on d- *and* l-*β-Hydroxy-β-phenylpropionic Acids. Interconversion of the Acids.*

Preliminary experiments indicated that a sulphito-chloride is produced by the action of thionyl chloride on the β-hydroxy-β-phenylpropionic acids, and that the change

$$C_6H_5\cdot CH(O\cdot SOCl)\cdot CH_2\cdot COCl \longrightarrow SO_2 + C_6H_5\cdot CHCl\cdot CH_2\cdot COCl$$

requires a fairly high temperature for its completion. The resulting β-chloro-β-phenylpropionyl chloride also contained a large amount of cinnamoyl chloride due to the elimination of hydrogen chloride.

A mixture of *d*-β-hydroxy-β-phenylpropionic acid (8 grams) and thionyl chloride (20 grams) remained at the ordinary temperature for fifteen hours, and was then boiled for twenty minutes. After removal of the thionyl chloride, the residual oil was distilled under diminished pressure, when a large amount of gas was evolved. On re-distillation, a colourless, strongly refractive liquid (5 grams) was obtained, boiling at 137—137·5°/12 mm. It had $\alpha_D^{17\cdot5}$ +25·38° in a 50 mm. tube, and a halogen determination showed that it contained no less than 48 per cent. of cinnamoyl chloride. It was hydrolysed by moist ether, and 3·8 grams of lustrous, colourless leaflets were obtained, which were examined in ethyl-alcoholic solution:

$$l=2,\ c=3\cdot836,\ \alpha_D^{16}\ +2\cdot54°,\ [\alpha]_D^{16}\ +33\cdot1°.$$

This product was separated into two fractions by crystallisation from benzene. The crystals which separated consisted of β-chloro-β-phenylpropionic acid and cinnamic acid, the latter being present to the extent of 39 per cent.; in ethyl-alcoholic solution, the value $[\alpha]_D$ +21·0° for $c=4\cdot436$ was obtained. On evaporation of the mother liquor, the product gave $[\alpha]_D$ +44·7° for $c=5\cdot498$.

The action of water on these mixtures of cinnamic acid, *r*- and *d*-β-chloro-β-phenylpropionic acids, was next investigated. The product (1·3 grams) with $[\alpha]_D$ +21·0° was boiled with water (50 c.c.) for several hours; the odour of styrene was perceptible, and, on cooling, cinnamic acid (0·62 gram) separated. The latter was removed, and the hydroxy-acid extracted with ether in a continuous apparatus. After crystallisation of the product from benzene, 0·42 gram of hydroxy-acid was obtained (Found, C=64·9; H=6·1. Calc., C=65·0; H=6·1 per cent.); it melted at 95—102°, and was a mixture of *r*- and *l*-β-hydroxy-β-phenylpropionic acids. The optical activity was slight, but distinct. In ethyl-alcoholic solution:

$$l=0\cdot5,\ c=13\cdot8,\ \alpha_D\ -0\cdot24°,\ [\alpha]_D\ -3\cdot5°.$$

The homogeneous *l*-acid, according to McKenzie and Humphries (*loc. cit.*), has $[\alpha]_D$ $-18\cdot9°$.

This result was confirmed by the action of water on the product with $[\alpha]_D$ $+44\cdot7°$. One and a-half grams of this, when decomposed by water, gave 0·55 gram of cinnamic acid and 0·55 gram of crude hydroxy-acid, which, after crystallisation from benzene, amounted to 0·44 gram. (Found, C=65·0; H=6·15. Calc., C=65·0; H=6·1 per cent.) In ethyl-alcoholic solution, the latter acid was lævorotatory:

$$l=0\cdot5,\ c=15\cdot33,\ \alpha_D\ -0\cdot44°,\ [\alpha]_D\ -5\cdot7°.$$

The residue remaining in the flask after distillation of the chlorochloride in the preceding experiment solidified on cooling, and was purified by crystallisation from ethyl alcohol, from which it separated in very pale yellow needles, melting at 134°. Yield, 1·1 grams. The compound proved to be optically inactive, and insoluble in sodium hydroxide. It had the properties of cinnamic anhydride, which, according to Liebermann, melts at 133°. (Found, C=77·5; H=5·3. Calc., C=77·7; H=5·1 per cent.) Its molecular weight in benzene solution gave the value 266 (calc., 278). Its phenylhydrazide separated from a mixture of ethyl alcohol and water in yellow needles, m. p. 186—187°, whereas Wedekind (*Ber.*, 1901, **34**, 2075) gives 187°.

The conversion of the *l*-hydroxy-acid into its *d*-isomeride was also carried out. The oil resulting from the action of thionyl chloride (28 grams) on *l*-β-hydroxy-β-phenylpropionic acid (10 grams) was distilled twice, and, as in the preceding experiment, a large quantity of gas was evolved during the first distillation. The product (6 grams) had α_D^{21} $-13\cdot75°$ in a 50 mm. tube, and boiled at 145—147°/23 mm. The mixture of chloro-acid and cinnamic acid obtained from it amounted to 5 grams, and had $[\alpha]_D$ $-14\cdot3°$ in ethyl-alcoholic solution. The hydroxy-acid, obtained from this by the action of water, was separated from cinnamic acid, and then gave $[\alpha]_D$ $+3\cdot4°$ in ethyl-alcoholic solution.

The authors are indebted to the Government Grant Committee of the Royal Society for a grant in aid of this research.

Birkbeck College,
London.

CCXVII.—*The Relation between Residual Affinity and Chemical Constitution. Part II. Certain Compounds of Nitrogen.*

By HANS THACHER CLARKE (1851 Exhibition Scholar).

IN a previous communication (Trans., 1910, **97**, 416) an account was given of a study of the reactivity of the halogen atom in certain organic halogen compounds when allowed to react with alcoholic pyridine. In the present work an attempt has been made to examine the effects of chemical constitution in a series of simple aliphatic tertiary amines containing two nitrogen atoms by a study of their reactivity towards alcoholic benzyl chloride, under standard conditions, as well as by an examination of the refractive powers of the comparable members of this series. The results of the reaction-velocity measurements are more difficult to interpret than in the case of the halogen compounds; only those substances which are of similar constitution have therefore been directly compared, in order to avoid, so far as possible, the introduction of the indeterminable influence due to steric considerations, as well as those due to structure demonstrated by N. Menschutkin (*Ber.*, 1897, **30**, 2775, etc.).

In the course of an examination of the properties of diethoxythioxan,

$$\begin{array}{c}\mathrm{CH_2{\cdot}S{\cdot}CH_2} \\ \mathrm{EtO{\cdot}CH{-}O{\cdot}CH{\cdot}OEt}\end{array},$$

Dr. Smiles and the present author (Trans., 1909, **95**, 992) were led to the conclusion that the sulphur and oxygen atoms situated in the 1:4-position in the saturated cyclic system exercised a mutual influence on each other, as shown by subnormal reactivity and exalted refractive power. In order to ascertain whether this phenomenon is constant throughout the series of six-membered cyclic compounds containing unsaturated atoms in the 1 : 4-positions, an extensive examination of such compounds has been undertaken. In the present paper the question of the piperazines is discussed.

The dialkylpiperazines may be prepared by the interaction of two molecules of ethylene bromide with two molecules of a primary amine, in the presence of some agent which will eliminate halogen hydride:

$$2\mathrm{R{\cdot}NH_2} + 2\mathrm{C_2H_4Br_2} + 4\mathrm{KOH} = \mathrm{R{\cdot}N}\!\left\langle\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\right\rangle\!\mathrm{N{\cdot}R} + 4\mathrm{KBr} + 2\mathrm{H_2O}.$$

For purposes of comparison, the corresponding open-chain methyl derivatives of ethylenediamine were selected:

$$R\cdot N<\begin{matrix}CH_2\cdot CH_2\\ CH_3\ \ CH_3\end{matrix}>N\cdot R.$$

A comparison of the refractive powers of the two classes of compound is thus readily effected with a minimum possible error, merely by subtracting the atomic refractions of two hydrogen atoms from the dimethyl derivative.

In carrying out the reactivity measurements, equal volumes of an $N/2$-solution of benzyl chloride and an $N/4$-solution of the tertiary diamine (or an $N/2$-solution of the tertiary monoamine) in absolute alcohol were mixed and maintained at 56°, aliquot portions being withdrawn from time to time and titrated by Volhard's method with $N/25$-solutions of silver nitrate and potassium thiocyanate. Owing to the complicated nature of the reaction, velocity-constants were in general not obtainable; the results are therefore expressed graphically by plotting the percentage of quaternary ammonium salt formed against the time. For purposes of comparison, it may perhaps be convenient to quote the times necessary to bring about 10 per cent. of the complete reaction, assuming total combination to be in all cases possible.

The first series shows the relative reactivities of a simple tertiary amine, a tertiary diamine, and a disubstituted piperazine, these being selected so as to be as nearly as possible comparable:

		Time for 10 per cent. reaction.
Ethylpiperidine	$C_5H_{10}NEt$	40 mins.
Ethylenedipiperidine ...	$C_5H_{10}N\cdot CH_2\cdot CH_2\cdot NC_5H_{10}$...	2 hrs., 45 mins.
Diethylpiperazine	$EtN<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>NEt$	8 mins.

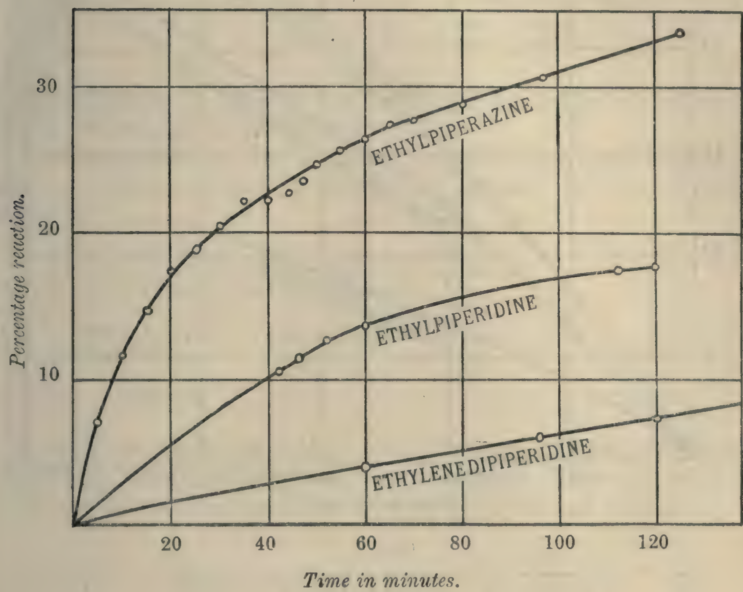
From this it is evident that ethylenedipiperidine, which may be regarded as a normal tertiary diamine, is far less reactive than diethylpiperazine, in which the unsaturated nitrogen atoms are situated in the 1:4-position in the ring. Ethylenedipiperidine is assumed to be normal, since the refractive power, 61·05 [as observed both by Brühl (*Zeitsch. physikal. Chem.*, 1895, **16**, 316) and the present author], agrees closely with the value calculated from the refractive power of methylpiperidine—31·58—as determined by Brühl (*loc. cit.*), and evaluated by the Lorentz-Lorenz formula:

	M_α (obs.).		M_α (calc.).	Δ.
Ethylenedipiperidine		$2C_5H_{10}NMe$......	63·16	
$C_5H_{10}N\cdot C_2H_4\cdot NC_5H_{10}$............		Less 2H	2·18	
	61·05		60·98	+0·07

The values of the atomic refractions are taken from Eisenlohr's paper (*Zeitsch. physikal. Chem.*, 1910, **75**, 585).

Further examples of piperazine derivatives were compared with the corresponding open-chain compounds:

FIG. 1.



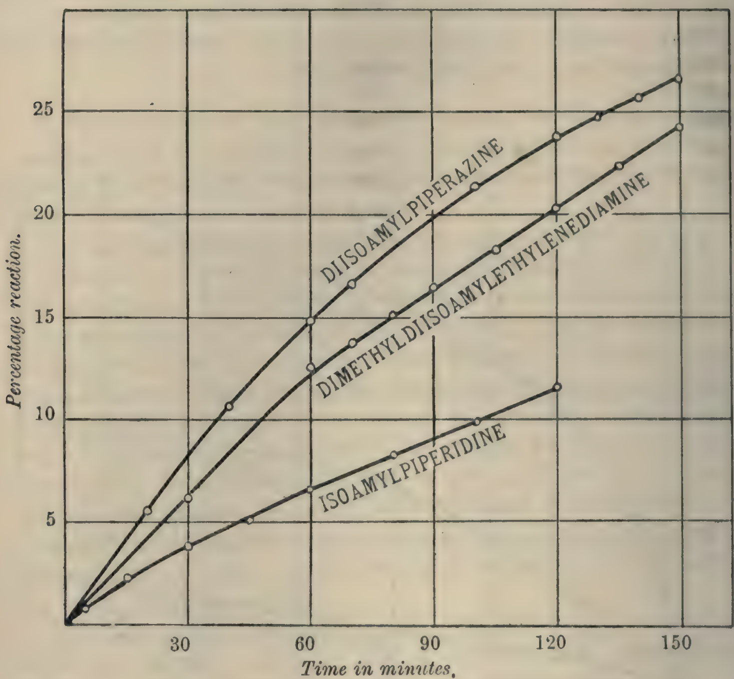
		Time for 10 per cent. reaction.
*iso*Amylpiperidine	$C_5H_{10}N{\cdot}C_5H_{11}$	1 hr., 40 mins.
Dimethyldi*iso*amylethylenediamine	$C_5H_{11}{\cdot}NMe{\cdot}C_2H_4{\cdot}NMe{\cdot}C_5H_{11}$...	48 mins.
Di*iso*amylpiperazine	$C_5H_{11}N\left<\begin{matrix}C_2H_4\\C_2H_4\end{matrix}\right>NC_5H_{11}$	37 mins.

		Time for 10 per cent. reaction.
Benzylpiperidine	$C_5H_{10}N{\cdot}CH_2Ph$....................	5 hrs., 10 mins.
Dibenzyldimethylethylenediamine	$CH_2Ph{\cdot}NMe{\cdot}C_2H_4{\cdot}NMe{\cdot}CH_2Ph$	17 hrs., 10 mins.
Dibenzylpiperazine	$CH_2Ph{\cdot}N\left<\begin{matrix}C_2H_4\\C_2H_4\end{matrix}\right>N{\cdot}CH_2Ph$...	12 hrs., 40 mins.

In both these cases the piperazine derivative is observed to be more reactive than a corresponding dimethyl derivative of ethylenediamine.

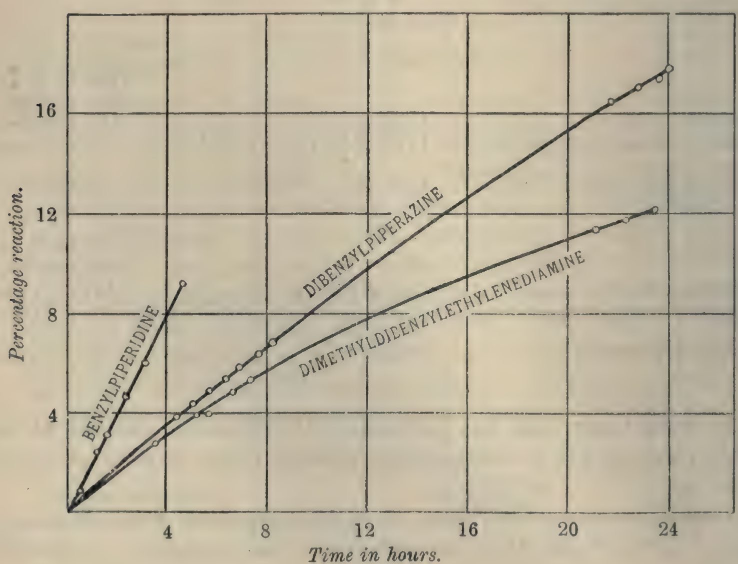
Refractive powers of these pairs of compounds were measured, and it was found that in each case the piperazine derivative

FIG. 2.



DIISOAMYLPIPERAZINE
DIMETHYLDIISOAMYLETHYLENEDIAMINE
ISOAMYLPIPERIDINE
Percentage reaction.
25
20
15
10
5
30
60
90
120
150
Time in minutes.

FIG. 3.



BENZYLPIPERIDINE
DIBENZYLPIPERAZINE
DIMETHYLDIBENZYLETHYLENEDIAMINE
Percentage reaction.
16
12
8
4
4
8
12
16
20
24
Time in hours.

exhibited a small but distinct exaltation, which is of the same order of magnitude as that observed for diethoxythioxan (+0·40).

	M_α (obs.).	M_α (calc.).	Δ.
Dimethyldi*iso*amylethylenediamine	74·12	—	—
Di*iso*amylpiperazine	72·46	71·94	+0·52
Dibenzyldimethylethylenediamine	85·52	—	—
Dibenzylpiperazine	83·83 (mean of three observations)	83·34	+0·49

Benzylpiperidine was also examined, and the value 55·65 observed for the molecular refractive power.

The calculation of the refractive power of the piperazines from that of the open-chain compound is effected in the ordinary manner.

	M_α.
Value for dimethyldi*iso*amylethylenediamine	74·12
Less value for two hydrogen atoms	2·18
Calculated value for di*iso*amylpiperazine	71·94
Observed ,, ,, ,,	72·46
Difference	+0·52

It may be noted that the value observed for benzylpiperidine (55·65) is normal, there being only a slight difference from the value calculated from those of methylpiperidine and toluene:

	M_α.
Methylpiperidine	31·58
Toluene	30·79
	60·37
Less $CH_2 + 2H$	6·78
Benzylpiperidine (calc.)	55·59
,, (obs.)	55·65
Difference	+0·06

The refractive powers of the corresponding phenyl open-chain and piperazine derivatives were determined, and the observed values compared with that of dimethylaniline (Brühl, *Zeitsch. physikal. Chem.*, 1895, **16**, 220):

	M_α (obs.).	M_α (calc.)	Δ.
Dimethylaniline, NMe_2Ph	40·38		
Diphenyldimethylethylenediamine, $NMePh\cdot CH_2\cdot CH_2\cdot NMePh$	78·65 (mean of two observations)	78·58	+0·07
Diphenylpiperazine, $PhN<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>NPh$	77·52 (mean of two observations)	76·47	+1·05

Diphenyldimethylethylenediamine is optically normal when compared with dimethylaniline:

	M_α.
Twice value for dimethylaniline (40·38)	80·76
Less value for two hydrogen atoms..............................	2·18
Calculated value for diphenyldimethylethylenediamine	78·58
Observed ,, ,, ...	78·65
Difference.........	+0·07

The value for diphenylpiperazine is directly calculated from that observed for diphenyldimethylethylenediamine.

In all the above instances it will be observed that the piperazine compound exhibits a small but well-defined optical exaltation, while from the case of the phenyl derivatives it is evident that Brühl's rule—that ring-formation is without effect on refractive power—may break down when unsaturated atoms are situated in certain positions in the ring. Although the inferences from the reactivity measurements in the piperazine series as compared with the open-chain methyl compounds must be drawn with all reserve on account of indeterminable steric and other influences, it may doubtless legitimately be concluded from the above evidence that the nitrogen atoms in piperazine compounds exert a mutual influence with the effect of increasing their reactivity and exalting their refractive power.

An attempt has also been made to detect influences ascribable to "space conjugation." This phenomenon was first observed by Hilditch (Trans., 1909, **95**, 1578), who found that anomalous optical rotatory power occurred in active esters and salts of saturated aliphatic dicarboxylic acids in which the carboxyl groups were in the 1:5- and 1:6-positions in a normal chain.

The reactivity towards benzyl chloride of a series of derivatives of piperidine in which the nitrogen atoms were separated by one, two, and three methylene groups:

$$C_5H_{10}N\cdot[CH_2]_n\cdot NC_5H_{10},$$

was observed. Monomethylenedipiperidine was found to be highly reactive; ethylenedipiperidine fell to a far lower value, which was noticeably increased in the case of trimethylenedipiperidine:

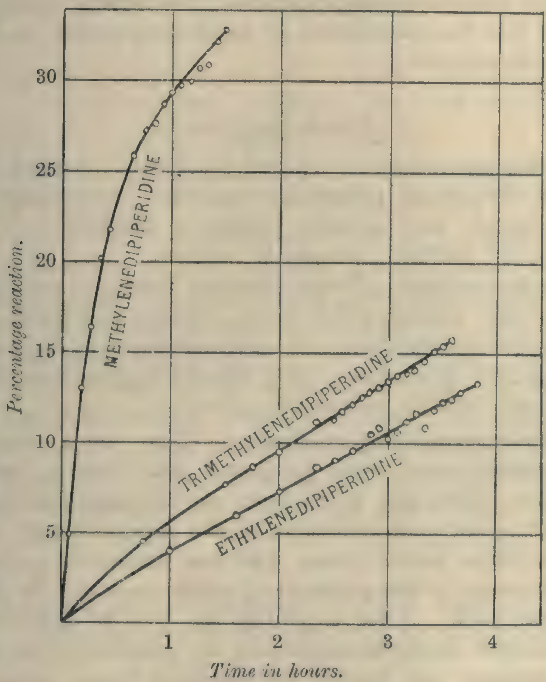
		Time for 10 per cent. reaction.
Methylenedipiperidine,	$C_5H_{10}N\cdot CH_2\cdot NC_5H_{10}$	7 mins.
Ethylenedipiperidine,	$C_5H_{10}N\cdot CH_2\cdot CH_2\cdot NC_5H_{10}$	2 hrs., 46 mins.
Trimethylenedipiperidine,	$C_5H_{10}N\cdot CH_2\cdot CH_2\cdot CH_2\cdot NC_5H_{10}$	2 hrs., 8 mins.

Several attempts were made to prepare tetra- and penta-methylenedipiperidine, but without success. On condensing $\alpha\epsilon$-dichloropentane with even a large excess of piperidine, the principal yield was

apparently the bicyclic quaternary ammonium chloride; only a very small quantity of an oil being obtained, which boiled above 300° under atmospheric pressure, and was insufficient for further purification. The quaternary chloride was not isolated.

From the above results it may be assumed that the two nitrogen atoms in methylenedipiperidine affect each other by virtue of their situation on the same carbon atom, in a manner similar to that of the halogen compounds described in a previous communication. Ethylenedipiperidine, in which the nitrogen atoms are situated

FIG. 4.



relatively in the 1:4-positions in the chain, may be regarded as normal. In trimethylenedipiperidine the nitrogen atoms are in the critical 1:5-position, and may be assumed to come into close proximity during their possible oscillations. This compound exhibits a reactivity above that of ethylenedipiperidine, so that it may without doubt justly be inferred that the spacial proximity induces the increased reactivity. The abnormality may be regarded as of the same type as that evinced by the piperazines, while the high reactivity of methylenedipiperidine may be attributed to a different cause.

The refractive powers of the derivatives of piperidine were measured, the following values being obtained:

	M_α.
Methylenedipiperidine	56·30
Ethylenedipiperidine	61·05
Trimethylenedipiperidine	65·62

Taking ethylenedipiperidine as the standard, and deducting or adding the refraction of the methylene group (4·60), methylenedipiperidine appears to be slightly depressed (−0·15), whilst trimethylenedipiperidine is almost exactly normal (−0·03). Refractive power therefore tends to throw no further light on the exalted reactivity of trimethylenedipiperidine. The author intends to enter more fully into the phenomena of space conjugation in a study of compounds of sulphur.

Experimental.

Methylenedipiperidine.—Prepared by Kraut's method (*Annalen*, 1890, **258**, 109) from piperidine and the condensation product of formaldehyde and sodium hydrogen sulphite. B. p. 235°. $D_4^{16·5}$ 0·9168, $n_\alpha^{16·5}$ 1·47903; whence $M_\alpha = 56·30$.

Ethylenedipiperidine.—From ethylene bromide and piperidine. B. p. 263°. $D_4^{16·5}$ 0·9236, $n_\alpha^{16·5}$ 1·48720; whence $M_\alpha = 61·05$.

Trimethylenedipiperidine.—From trimethylene bromide and piperidine. B. p. 278° [Töhl (*Ber.*, 1895, **28**, 2214) gives b. p. 274—275°]. D_4^{17} 0·9175, n_α^{17} 1·48520; whence $M_\alpha = 65·62$.

s-*Dimethyldi*iso*amylethylenediamine.*—Four molecular proportions of methyl*iso*amylamine [prepared by Störmer and Lepel's method (*Ber.*, 1896, **29**, 2118) from *iso*valeraldehyde and methylamine, with subsequent reduction of the product] were treated in alcoholic solution under reflux with one molecular proportion of ethylene bromide in the presence of sodium acetate for four hours on the water-bath. After expelling the bulk of the alcohol and some unchanged methyl*iso*amylamine by distillation on the water-bath, the product was treated with aqueous alkali, extracted with ether, and the ethereal extract fractionally distilled under diminished pressure. The pure product was obtained in good yield as a colourless oil, boiling at 130—131°/18 mm., insoluble in water, miscible with organic liquids, which rapidly absorbs carbon dioxide from the atmosphere, with formation of a solid product:

0·0826 gave 0·2222 CO_2 and 0·1050 H_2O. C = 73·37; H = 14·19.

$C_{14}H_{32}N_2$ requires C = 73·68; H = 14·03 per cent.

$D_4^{19·2}$ 0·8083, $n_\alpha^{19·2}$ 1·43855; whence $M_\alpha = 74·12$.

*Di*iso*amylpiperazine.*—Equimolecular proportions of *iso*amylamine and ethylene bromide in alcoholic solution were warmed on the

water-bath under reflux for eight hours, with occasional addition of alcoholic potassium hydroxide in quantities just sufficient to remove ionisable bromine as a precipitate of potassium bromide. On completion of the reaction the mixture was filtered, the filtrate rendered faintly acid with hydrochloric acid, and the alcohol evaporated. The residue was dissolved in water, extracted with a small quantity of ether, then rendered strongly alkaline, and again extracted with ether. The ethereal solution, after being dried, was freed from ether, and the residue fractionally distilled under diminished pressure. The pure *di*iso*amylpiperazine* was obtained in poor yield as a colourless oil, boiling at 136—137°/18 mm., insoluble in water, miscible with organic liquids, and strongly basic:

0·1048 gave 0·2840 CO_2 and 0·1273 H_2O. C=73·91; H=13·49.

$C_{14}H_{30}N_2$ requires C=74·34; H=13·28 per cent.

D_4^{20} 0·83603, n_a^{20} 1·44860; whence M_a=72·46.

Benzylpiperidine.—From benzyl chloride and piperidine. B. p. 245°. D_4^{16} 0·9625, n_a^{16} 1·52420; whence M_a=55·65.

s-*Dibenzyldimethylethylenediamine*.—Four molecular proportions of benzylmethylamine were warmed for five hours on the water-bath under reflux with one molecular proportion of ethylene bromide in alcohol in presence of sodium acetate. The mixture was then filtered, the alcohol expelled on the water-bath, and the residue treated with concentrated aqueous sodium hydroxide and extracted with ether. The extract, after being dried, was freed from ether, and the residue distilled under diminished pressure. The fraction boiling above 195°/10 mm. was collected separately, and redistilled, when the pure product was obtained as a pale yellow oil, boiling at 198°/10 mm., insoluble in water, and miscible with organic liquids:

0·0981 gave 0·2902 CO_2 and 0·0804 H_2O. C=80·67; H=9·16.

$C_{18}H_{24}N_2$ requires C=80·59; H=8·95 per cent.

$D_4^{18\cdot8}$ 0·9717, $n_a^{18\cdot8}$ 1·53244; whence M_a=85·52.

Dibenzylpiperazine.—Two samples were prepared; one from benzyl chloride and piperazine, and one from ethylene bromide and benzylamine in presence of alcoholic potassium hydroxide. In both cases the product was distilled under diminished pressure, and then recrystallised from alcohol. It melts at 92°.

I.—*In Alcohol.*

Solvent: $D^{18\cdot6}$ 0·79982; $n^{18\cdot6}$ 1·36138; wt. 3·3497.
Solution: D^{18} 0·81309; n^{18} 1·37235; wt. 3·5800.

M_a=83·88.

II.—*In Benzene.*

Solvent: D^{22} 0·87605; n^{22} 1·49484; wt. 1·9454.
Solution: D^{22} 0·89536; n^{22} 1·50360; wt. 2·2495.

$M_\alpha = 83 \cdot 72.$

III.—*In Benzene.*

Solvent: D^{22} 0·87605; n^{22} 1·49484; wt. 2·2425.
Solution: D^{22} 0·89215; n^{22} 1·50221; wt. 2·5225.

$M_\alpha = 83 \cdot 90.$

s-*Diphenyldimethylethylenediamine.*—Prepared by Dunlop and Jones' method (Trans., 1909, **95**, 418) from ethylene bromide and an excess of monomethylaniline at 100°. The product was distilled under diminished pressure, and then recrystallised from alcohol. It melted at 47·5°.

I.—*In Benzene.*

Solvent: D^{22} 0·87605; n^{22} 1·49484; wt. 3·1770.
Solution: D^{22} 0·89334; n^{22} 1·50536; wt. 3·5420.

$M_\alpha = 78 \cdot 54.$

II.—*In Benzene.*

Solvent: D^{22} 0·87605; n^{22} 1·49484; wt. 1·9015.
Solution: $D^{21 \cdot 5}$ 0·89594; $n^{21 \cdot 5}$ 1·50719; wt. 2·1476.

$M_\alpha = 78 \cdot 77.$

Diphenylpiperazine.—Prepared by the interaction of ethylene bromide and aniline in the presence of sodium carbonate. The product was distilled under diminished pressure, and recrystallised from alcohol. It melted at 163°.

I.—*In Benzene.*

Solvent: D^{22} 0·87605; n^{22} 1·49484; wt. 2·9416.
Solution: D^{21} 0·88517; n^{21} 1·50028; wt. 3·0895.

$M_\alpha = 77 \cdot 42.$

II.—*In Benzene.*

Solvent: D^{22} 0·87605; n^{22} 1·49484; wt. 3·6060.
Solution: D^{22} 0·88315; n^{22} 1·49915; wt. 3·7423.

$M_\alpha = 77 \cdot 63.$

Conclusions.

(1) The nitrogen atoms in *N*-substituted piperazines exert a mutual influence, occasioning optical exaltation.

(2) Tervalent nitrogen atoms in the "critical" positions in normal

chain compounds exert a similar mutual influence, but no optical anomaly has been detected in such substances.

(3) The reactivity towards organic halogen compounds of nitrogen atoms exerting such mutual influence is thereby increased.

The author desires to thank Dr. Smiles for valued advice and encouragement, and to express his gratitude to the Research Fund Committee of the Society for a grant in aid of the work.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE, LONDON.

CCXVIII.—*The Temperature-coefficient of the Electrical Conductivity of Hydrogen Chloride in Alcoholic Solution.*

By JAMES RIDDICK PARTINGTON.

IN a recent communication (Lapworth and Partington, this vol., p. 1417), the existing data for the conductivity of alcoholic hydrogen chloride were discussed, and it was remarked that the values of different observers were not in agreement. The conductivities at 25° were re-determined, and found to lie close to the values of Goldschmidt and Udby (*Zeitsch. Elektrochem.*, 1909, **15**, 5), except at high dilutions, when they were consistently lower than the latter. The value of λ_∞ at 25° was fixed at 66·5.

The number 43·10, recorded by Baly, Burke, and Marsden (Trans., 1909, **95**, 1100) as the result of experiments at 15° (of which no details are given), together with the temperature-coefficient of Völlmer (*Ann. Physik*, 1894, [iii], **52**, 328), leads to a value of λ_∞ at 25° which is certainly considerably lower than any other recorded value. It was therefore thought desirable to determine the conductivities at 0° and 18° (these temperatures being more conveniently maintained than 15°) with the purpose of finding whether, possibly, there might be some abnormality in the temperature-coefficient, and also of obtaining data on the electrical relations of hydrogen chloride which will be required in further investigations now in progress in this laboratory.

The apparatus consisted of cells of three different sizes, with platinised platinum electrodes, and closed with carefully ground glass stoppers. The constants were determined at 25° by means

of $N/10$-potassium chloride solution, the specific conductivity of which was taken as $k = 0{\cdot}01288$ mho.

Resistance measurements were made by means of a Nalder pattern Wheatstone bridge, with a small induction coil and telephone.

Alcoholic hydrogen chloride solutions were prepared and kept in the manner described in a previous communication (Trans., 1910, **99**, 1420).

The cells were cleaned with nitric acid and distilled water, and then carefully dried in an air-oven before each measurement. They were filled as rapidly as possible from a pipette, quickly stoppered, and the stopper covered with Faraday cement. The filling and closing of the cell must not occupy more than half a minute, otherwise the entrance of atmospheric moisture vitiates the results. The leads were joined through stout rubber tubing to glass tubes with mercury connexions, which were sealed into the sides of the cell, so that the whole could be sunk in a thermostat (compare Partington, this vol., p. 470), or immersed in clean, pounded ice, as required. The solutions could be kept for several days in carefully closed flasks in full daylight without altering in conductivity, but if allowed to remain for a day in the cell (that is, in contact with platinum), their conductivities decreased, and the solutions gave the Schiff reaction for aldehydes (compare Cohen, *Zeitsch. physikal. Chem.*, 1898, **25**, 1; Lapworth and Partington, this vol., pp. 1422, 1426). Measurements with solutions of very different concentrations, and extending over several hours, showed that steady values of the conductivity were reached after half an hour at 0°, and fifteen minutes at 18°; with very dilute solutions the conductivities changed appreciably after about twelve hours. The cells were frequently shaken during the measurements.

In the tables below are given (I) the concentrations in gram-molecules per litre, (II) the observed resistances in ohms, (III) the cell constants, (IV) the molecular conductivities, (V) the values of the latter from the smoothed curves. The values of λ_{∞} were obtained by the graphical method described in the previous communication. The values at the highest dilution were corrected for the conductivity of the specimen of alcohol used; for all other concentrations this correction was inappreciable.

Table I.

Conductivities at 0°.

(I.)	(II.)	(III.)	(IV.)	(V.)
0·850	39·5	0·42345	12·61	13·55
0·850	39·0	0·42345	12·77	
0·8446	39·58	0·40314	12·06	13·60
0·8446	39·24	0·40314	12·16	
0·585	47·70	0·40314	14·45	15·50
0·4086	58·92	0·40314	16·75	17·0
0·4086	58·80	0·40314	16·78	
0·2495	81·00	0·40314	19·95	19·95
0·115	158·00	0·42345	23·30	23·30
0·0853	40·15	0·08468	24·73	24·77
0·0853	40·00	0·08468	24·82	
0·0342	400·00	0·40314	28·86	28·86
0·0342	399·6	0·40314	28·89	
0·0342	400·3	0·40314	28·84	
0·023	578·1	0·40314	30·32	30·32
0·01079	338·8	0·12624	34·53	34·45
0·01079	323·5	0·12624	36·17*	
0·01079	332·75	0·12624	35·16	
0·01079	326·0	0·12624	35·89*	
0·01079	337·0	0·12624	34·72	
0·001079	2693·0	0·12624	42·64	40·35
0·001079	2600·0	0·12624	42·35	
0·001079	2685·0	0·12624	42·80	
0·001079	2720·0	0·12624	40·76	
0·00	151000·0	0·12624		

λ_∞ at 0° = 46·50 (extrapolated).

Table II.

Conductivities at 18°.

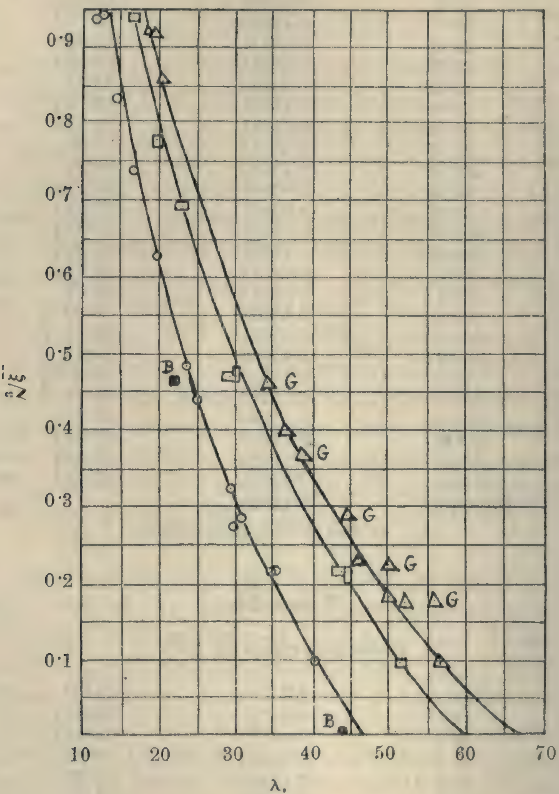
(I.)	(II.)	(III.)	(IV.)	(V.)
0·850	46·0	0·6472	16·55	16·45
0·850	46·6	0·6472	16·34	
0·4840	44·0	0·12624	19·83	20·50
0·3363	82·3	0·42345	23·38	23·38
0·1079	122·9	0·42345	31·93	31·50
0·1059	134·0	0·42345	29·73	31·55
0·1059	134·5	0·42345	29·73	
0·01059	270·0	0·12624	44·15	44·15
0·01059	270·0	0·12624	44·15	
0·001059	2190·0	0·12624	51·46	51·47
0·001059	2190·0	0·12624	51·46	
0·001059	2170·0	0·12624	51·96*	
0·001059	2150·0	0·12624	51·49	
0·00	1610000·0	0·12624	—	

λ_∞ at 18° = 60·00 (extrapolated).

(All values marked with asterisks were rejected in calculating the mean values.)

These results, along with those at 25° recorded in the previous paper, are represented graphically in Fig. 1, where λ is plotted against the cube root of the concentration. The values of

Goldschmidt and Udby (G) at 25°, and of Baly, Burke, and Marsden (B) at 15°, are added for comparison. The latter values are evidently much too small, and their position with respect to the curves makes it probable that they contain a large constant



⊙ *Conductivities at* 0°.
□ ,, ,, 18°.
△ ,, ,, 25°.

error—possibly some arithmetical inaccuracy in connexion with the cell-constant. As these observers give no details, it is not possible to hazard any more definite explanation of the discrepancy.

The Temperature-coefficient of λ_∞.

If we assume that the molecular conductivity is a linear function of temperature:

$$\lambda = \lambda_0(1 + \alpha\theta),$$

where θ=temperature Centigrade, a=temperature-coefficient, we find, from the three values:

$$(a)\ \lambda_\infty = 46{\cdot}5 \text{ when } \theta = 0$$
$$(b)\ \lambda_\infty = 60{\cdot}0 \quad ,, \quad \theta = 18$$
$$(c)\ \lambda_\infty = 66{\cdot}5 \quad ,, \quad \theta = 25,$$

the following values of a_∞:

$$(a) \text{ and } (b)\ a_\infty = 0{\cdot}0185$$
$$(a)\ ,,\ (c)\ a_\infty = 0{\cdot}0172$$
$$\therefore \text{ Mean } a_\infty = 0{\cdot}0178.$$

Summary.

The conductivities of alcoholic solutions of hydrogen chloride have been determined at 0° and 18°. The results of these experiments, together with those of previous experiments at 25°, have led to the following values for the limiting molecular conductivities and the temperature-coefficient a of the latter:

$$\lambda_\infty \text{ at } 0° = 46{\cdot}50$$
$$\lambda_\infty\ ,,\ 18° = 60{\cdot}00$$
$$\lambda_\infty\ ,,\ 25° = 66{\cdot}50$$
$$a_\infty\,(\text{mean}) = 0{\cdot}0178.$$

In conclusion, the author desires to thank Dr. A. Lapworth for the interest he has taken in the progress of the research.

SCHUNCK LABORATORY,
UNIVERSITY OF MANCHESTER.

CCXIX.—*The Absorption Spectra of the Nitration Products of Dimethyl-*p*-toluidine.*

By GILBERT T. MORGAN and ARTHUR CLAYTON.

IN continuance of their earlier investigations on the nitration of dimethyl-*p*-toluidine (Trans., 1905, **87**, 947; 1910, **97**, 2645), the authors have endeavoured to complete the series of nitro-derivatives of this tertiary base with the object of studying the effect of successive nitration on the colours and absorption spectra of these products.

Six of the nine theoretically possible nitro-derivatives of dimethyl-*p*-toluidine are known at present, together with several secondary nitration products (nitrosoamines and nitroamines), and an account

of the work is now put forward, inasmuch as the absorption spectra of polynitrated aromatic amines and their derivatives have not hitherto received much attention.

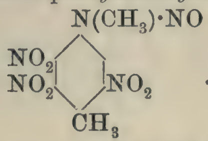
2 : 3 : 6-*Trinitrodimethyl*-p-*toluidine* (Formula VII).

A solution of one part of 2 : 6-dinitrodimethyl-*p*-toluidine in nine parts of concentrated sulphuric acid was diluted with fifteen parts of water, and the pasty mass thus produced treated with two to three parts of nitric acid (D 1·4), the mixture being heated at 95° for about ten minutes. The product, which was crystallised repeatedly from alcohol, separated in scarlet, flattened needles or plates, and melted at 137°:

0·1116 gave 0·1652 CO_2 and 0·0399 H_2O. C = 40·37; H = 3·97.
0·1005 ,, 18·4 c.c. N_2 at 22° and 760 mm. N = 20·75.
$C_9H_{10}O_6N_4$ requires C = 40·00; H = 3·70; N = 20·74 per cent.

The constitution of 2 : 3 : 6-*trinitrodimethyl*-p-*toluidine* is sufficiently indicated by the preparation of the base from 2 : 6-dinitrodimethyl-*p*-toluidine (Trans., 1910, **97**, 2645), as only one trinitro-derivative is theoretically possible.

2 : 3 : 6-*Trinitro*-p-*tolylmethylnitrosoamine*,



The action of highly concentrated nitric and sulphuric acids at high temperatures on the foregoing trinitro-base led to decomposition; milder treatment furnished the nitrosoamine with elimination of a methyl group from the tertiary amine radicle.

The pasty mass obtained by adding ten parts of water to the solution of one part of the trinitro-compound in nine parts of concentrated sulphuric acid was warmed for a short time at 80° with three parts of nitric acid (D 1·4), until the colour changed from red to yellow. The product was precipitated by ice-water, and crystallised from glacial acetic acid:

0·1403 gave 0·1751 CO_2 and 0·0366 H_2O. C = 34·03; H = 2·89.
0·0822 ,, 17·3 c.c. N_2 at 19° and 766 mm. N = 24·33.
$C_8H_7O_7N_5$ requires C = 33·68; H = 2·46; N = 24·56 per cent.

2 : 3 : 6-*Trinitro*-p-*tolylmethylnitrosoamine* crystallises in yellow needles, melting at 162—163°, and giving the Liebermann reaction; it can also be prepared by heating the trinitro-base directly with a mixture of nitric acid (D 1·4) and 60 per cent. sulphuric acid.

2:5-*Dinitro*-p-*tolylmethylnitrosoamine* (Formula VIII).

A mixture of 2:5-dinitrodimethyl-*p*-toluidine (one part), 60 per cent. sulphuric acid (forty parts), and nitric acid (five parts, D 1·4) was heated for one hour at 100°, and the product crystallised from alcohol:

0·1672 gave 0·2460 CO_2 and 0·0596 H_2O. C = 40·13; H = 3·94.
0·1233 „ 25·0 c.c. N_2 at 18° and 760 mm. N = 23·42.
$C_8H_8O_5N_4$ requires C = 40·00; H = 3·33; N = 23·33 per cent.

2:5-*Dinitro*-p-*tolylmethylnitrosoamine* crystallises in pale yellow needles, melting at 126—127°; it is identical with one of the two nitrosoamines obtained by Pinnow from methyl-*p*-toluidine (*Ber.*, 1897, **30**, 840).

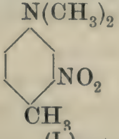
Action of Nitric Acid on 3:5-*Dinitrodimethyl*-p-*toluidine.*—This dinitro-base, when treated with mixtures of concentrated nitric and sulphuric acids at temperatures below 80°, remained unchanged; at higher temperatures a methyl group was eliminated, often with extreme violence owing to the formation of explosive methyl nitrate. The only definite products were 3:5-dinitro-*p*-tolylmethylnitrosoamine (m. p. 128°; Formula IX; compare Romburgh, *Ber.*, 1896, **29**, 1016) and the corresponding nitroamine. There was no indication of further nitration in the ring without elimination of a methyl group.

3:5-Dinitro-*p*-tolylmethylnitroamine (m. p. 138°; Formula X) was also prepared by the action of concentrated nitric acid (D 1·5) on the foregoing nitrosoamine (compare Gattermann, *Ber.*, 1885, **18**, 1482; Romburgh, *loc. cit.*; and Reverdin, *J. pr. Chem.*, 1911, [ii], **83**, 167).

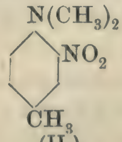
Absorption Spectra.

The absorption spectra of the nitrated dimethyl-*p*-toluidines and nitrated *p*-tolylmethylnitrosoamines were examined in absolute alcoholic solutions. The source of light was an iron arc, and a quartz spectrograph of high dispersive power was employed.

2-Nitrodimethyl-*p*-toluidine (m. p. 37°; Formula I; compare Trans., 1905, **87**, 947) was compared with its isomeride, 3-nitrodimethyl-*p*-toluidine (m. p. 25°; Formula II; Pinnow, *Ber.*, 1895, **28**, 3039), which was readily prepared in a solid form from its recrystallised sulphate. The absorption of the latter base has already been described by Baly, Tuck, and Marsden (Trans., 1910, **97**, 581):



(I.)



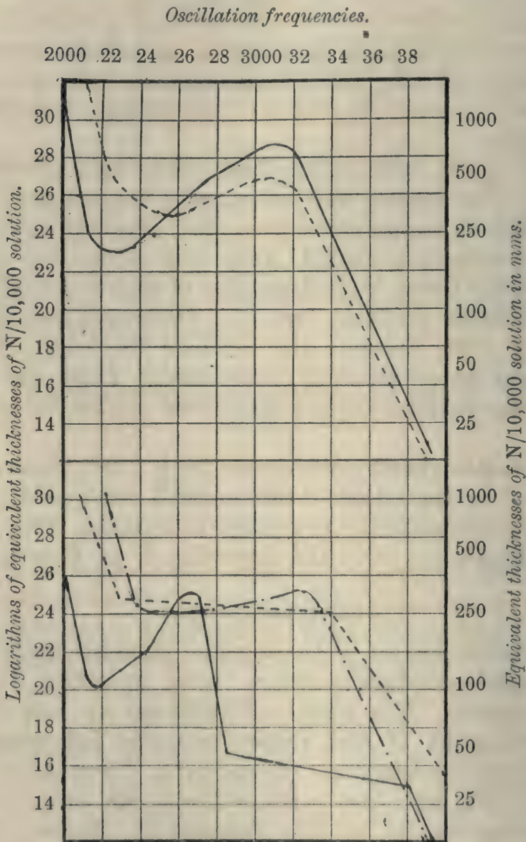
(II.)

The absorption curves of these two isomerides have the same general form, thus indicating similarity in constitution. The chief

FIG. 1.

Upper curves:

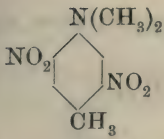
Full curve ——— 3-*Nitrodimethyl*-p-*toluidine.*
Dotted ,, - - - - - 2-*Nitrodimethyl*-p-*toluidine*



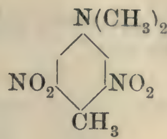
Lower curves:

Full curve ——— 2 : 5-*Dinitrodimethyl*-p-*toluidine.*
Dotted ,, - - - - - 3 : 5-*Dinitrodimethyl*-p-*toluidine.*
Dot and dash - — - 2 : 6-*Dinitrodimethyl*-p-*toluidine.*

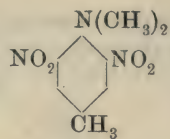
difference is that the absorption band of the ortho-nitroamine is nearer the red end (head of curve $1/\lambda$ 2290), and more persistent than the band ($1/\lambda$ 2560) of the meta-nitroamine:



(III.)



(IV.)



(V.)

2:5-Dinitrodimethyl-*p*-toluidine (Morgan and Clayton, *loc. cit.*), which contains its two nitro-groups unsymmetrically arranged with respect to the aminic radicle, shows an absorption band ($1/\lambda$ 2160) narrower than, but still comparable with, the bands exhibited by the two foregoing mononitro-bases. The remainder of the absorption curve (Fig. 1) departs from the form characteristic of aromatic mononitroamines in showing a very rapid change of absorption at certain dilutions, a step-out making its appearance at $1/\lambda$ 2820—$1/\lambda$ 3800.

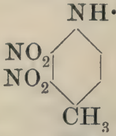
2:6-Dinitrodimethyl-*p*-toluidine (Morgan and Clayton, *loc. cit.*) gives a curve differing very considerably from those of the foregoing nitrated amines, and also from those of all other aromatic nitroamines which have been previously studied (compare Baly, Tuck, and Marsden, *loc. cit.*). The absorption band (head $1/\lambda$ 2550) is broadened and flattened almost to extinction, the remainder of the curve being comparable with that of 2-nitrodimethyl-*p*-toluidine.

The 2:6-dinitro-base differs from the 2:5-dinitro-isomeride in containing its two nitro-groups symmetrically disposed with regard to the basic group, a fact which suggests that symmetry of the molecule may play an important part in diminishing the selective absorption exercised by the compound. This hypothesis is supported by the behaviour of 3:5-dinitrodimethyl-*p*-toluidine (m. p. 99—100°; Pinnow, *Ber.*, 1898, **31**, 2518). This base also contains its two nitro-groups in symmetrical positions with respect to the basic nitrogen, but in this instance they are both in ortho-, whereas in the former they are both in meta-positions. Since substituents in ortho-positions almost invariably affect each other more than when present in meta-positions, it is not surprising to find that the diminution of selective absorption attains its maximum in the case of 3:5-dinitrodimethyl-*p*-toluidine. The absorption band (Fig. 1) has disappeared, and is replaced by a step-out.

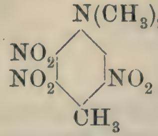
As it was not found possible to prepare 2:3-dinitrodimethyl-*p*-toluidine, the remaining isomeride of the above-mentioned bases, the corresponding 2:3-dinitromethyl-*p*-toluidine (Formula VI) was prepared and examined (Pinnow, *Ber.*, 1897, **30**, 833).

This comparison is quite justifiable, because Baly, Tuck, and Marsden (*loc. cit.*) have shown that in this group of nitro-compounds the mono- and di-methyl derivatives exhibit practically the same

absorption spectra, the only difference being that methylation shifts the absorption a little to the red:



(VI.)

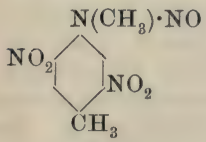


(VII.)

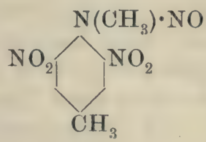
The substitution of a nitro-group in 2:6-dinitrodimethyl-*p*-toluidine to form 2:3:6-trinitrodimethyl-*p*-toluidine (VII) introduces into the molecule an element of dissymmetry which is manifested in the absorption curve (Fig. 2) by the reappearance of the band ($1/\lambda$ 2280), which, however, is comparatively shallow.

In 2:3-dinitromethyl-*p*-toluidine (VI), where the substituents are arranged consecutively, the maximum amount of dissymmetry is produced, and the absorption curve indicates a band ($1/\lambda$ 2280) which is the most persistent of any exhibited by this series of nitrated amines.

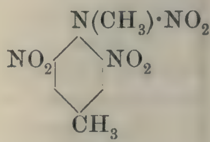
An examination of the absorption spectra of 2:5-dinitro- and 3:5-dinitro-*p*-tolylmethylnitrosoamines shows, however, that this effect of dissymmetry is exhibited only when the basic aminic group is present in the molecule. This basicity is considerably diminished by the replacement of one methyl group by a nitroso- or nitro-radicle:



(VIII.)



(IX.)



(X.)

The absorption curves of 2:5-dinitro-*p*-tolylmethylnitrosoamine (VIII) and 3:5-dinitro-*p*-tolylmethylnitrosoamine (IX) indicate a very similar general absorption (Fig. 2), although the former compound contains its nitro-groups unsymmetrically arranged with regard to the aminic nitrogen, whilst the nitro-groups of the latter isomeride are disposed symmetrically in this respect.

3:5-Dinitro-*p*-tolylmethylnitroamine (X) when first discovered was regarded as a trinitromethyl-*p*-toluidine (Gattermann, *loc. cit.*), but its absorption curve is quite comparable with those of the foregoing nitrosoamines, thus furnishing spectroscopic evidence in support of Romburgh's observation that one of the three nitro-groups is attached to nitrogen (*Rec. trav. chim.*, 1882, **3**, 404).

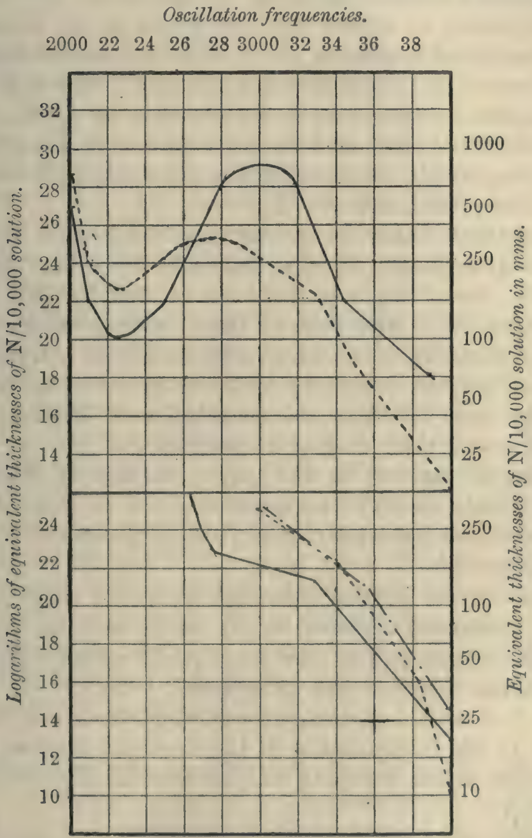
The Colour of Aromatic Nitroamines.

The introduction of an amino-group into the benzene nucleus involves a complete change in the absorption spectrum of this

FIG. 2.

Upper curves:

Full curve ——— 3 : 5-*Dinitromonomethyl*-p-*toluidine.*
Dotted ,, - - - - - 2 : 3 : 6-*Trinitrodimethyl*-p-*toluidine.*



Lower curves:

Full curve ——— 2 : 5-*Dinitro*-p-*tolylmethylnitrosoamine.*
Dotted ,, - - - - - 3 : 5-*Dinitro*-p-*tolylmethylnitrosoamine.*
Dot and dash - — - 3 : 5-*Dinitro*-p-*tolylmethylnitroamine.*

hydrocarbon. The seven small bands of benzene disappear, and the new spectrum exhibits one broad, well-defined band in the ultra-violet (Baly and Collie, Trans., 1905, **87**, 1343). The conversion

of colourless aniline into the yellow nitroanilines is not accompanied by any such marked alteration in the general character of the absorption, the change consisting mainly in a shift of the absorption band into the visible region of the spectrum, and in a persistence of the absorption at greater dilutions.

The question of relationship between the colour and constitution of benzenoid nitroamines is accordingly a special case of the general problem of the connexion between the selective absorption of aromatic bases and their chemical configuration.

It is customary to regard the nitro-group as the chromophor in nitroamines, but this effect is not specific, for other complexes play a similar part. In the aminocoumarins and their alkyl derivatives the unsaturated lactonic ring is the chromophor (Trans., 1904, **85**, 1230; 1910, **87**, 1350), and β-anthramine and di-*o*-aminostilbene exhibit colour in the absence of any substituent (*Annalen*, 1882, **212**, 57; *Ber.*, 1895, **28**, 1411).

The hypothesis that the colour of nitroanilines is due to a quinoid rearrangement of the molecule involving migration of hydrogen to the nitro-group, has been refuted by Baly, Tuck, and Marsden (*loc. cit.*), who showed that 3-nitro-*p*-toluidine and its methyl and dimethyl derivatives give absorption curves which are almost superposable, excepting that methylation shifts the band towards the red. Similar relationships were observed with the nitroanilines and their dialkyl derivatives.

With one nitro-group in the ring, variation in the orientation does not greatly modify the spectrum, but in general the band of the ortho- and para-derivatives is more persistent than that of the meta-isomeride.

As shown in the present communication, the effect produced by a second nitro-group depends largely on its position in relation to the aminic radicle and to the nitro-group already present. The question arises whether the exceptional form of the absorption curves of 2 : 6- and 3 : 5-dinitrodimethyl-*p*-toluidine is due to some alteration in the configuration of the aromatic nucleus consequent on the symmetrical grouping of the two nitro-groups about the basic radicle.

Kaufmann has suggested (*Ber.*, 1902, **35**, 3668) that nitro- and amino-derivatives of benzene contain respectively the aromatic nucleus in centric and para-quinonoid conditions, the latter corresponding with Dewar's benzene formula. In accordance with this view, one might expect that increase in the number of nitro-groups would result in a change from the spectrum of the nitroanilines to that exhibited by nitrobenzene. But the absorption curve of

2 : 3 : 6-trinitrodimethyl-*p*-toluidine is nearer to the characteristic nitroamino-form than that of 2 : 6-dinitrodimethyl-*p*-toluidine.

Moreover, Hantzsch has compared the spectrum of 3 : 5-dinitroaniline with that of 5-nitro-1 : 3-phenylenediamine, a base having an equally symmetric molecule, but a preponderance of amino-groups. The two curves are very similar, the bands occurring nearly in the same region of the spectrum, but, on the other hand, these absorption spectra are entirely different from that of 1 : 3 : 5-trinitrobenzene, which has no absorption band (*Ber.*, 1910, **43**, 1669).

It seems reasonable to infer that, in so far as mono-, di-, and tri-nitroamines are concerned, any change in the aromatic nucleus which may result from successive nitration is not such as can be indicated by differences in structural formulæ (compare Hartley, Trans., 1885, **47**, 693). This conclusion has also been reached by Hantzsch (*loc. cit.*), who regards the nitroanilines and their alkyl derivatives as having the conventional formula, but with the nitro-groups linked by subsidiary valencies to the hydrogen or alkyl radicles of the amino-group.

The fact that the character of the absorption is altered completely by the saturation of the aminic group suggests, however, that the predominant factor is the residual affinity of basic nitrogen. The shift of the absorption into the visible region of the spectrum may be regarded as due to a chemical change of the nature of internal salt formation, since it is independent of the relative positions of the amino- and nitro-groups involved. When the residual affinity of the basic nitrogen is directed wholly towards one nitro-group or towards two contiguous nitro-groups, then the molecule becomes unevenly strained, and a well-defined absorption band is manifested. If, however, this residual affinity is divided between two similarly situated nitro-groups, then the atomic stresses may be supposed to be more evenly distributed in the molecule, with the result that less selective absorption takes place.

The authors desire to express their thanks to Dr. W. B. Tuck for his kind assistance in preparing the photographs and absorption curves, and to the Research Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

THE ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

CCXX.—*Decomposition of Hydrazides and Hydrazones by Heat.*

By FREDERICK DANIEL CHATTAWAY, CHARLES LINAEUS CUMMING, and BERNARD HOWELL WILSDON.

IN continuation of an investigation of the behaviour of hydrazines at a high temperature, the reactions which take place when various hydrazides and hydrazones are heated have been studied.

When a phthalylhydrazide is heated, vigorous action accompanied by the evolution of heat sets in at a definite temperature, nitrogen and ammonia are liberated, and a phthalanil is produced, thus:

$$3C_6H_4{<}{}^{CO}_{CO}{>}N\cdot NHR = 3C_6H_4{<}{}^{CO}_{CO}{>}NR + N_2 + NH_3.$$

When a hydrazone is heated, two main reactions take place, resulting in the formation of an unsaturated hydrocarbon, nitrogen, and a saturated hydrocarbon, thus:

$$2CHR{:}N\cdot NHR' = CHR{:}CHR + 2N_2 + 2R'H,$$

and in the formation of an alkylideneaniline, nitrogen, and ammonia, thus:

$$3CHR{:}N\cdot NHR = 3CRH{:}NR' + N_2 + NH_3.$$

The two reactions proceed simultaneously, a somewhat larger amount of the hydrazone as a rule undergoing the latter decomposition.

EXPERIMENTAL.

Decomposition of Phthalylphenylhydrazide by Heat.

Phthalylphenylhydrazide when crystallised from alcohol, which is the most convenient solvent to employ, is usually obtained as a mixture of two polymorphic modifications; the crystals of one are bright yellow, those of the other almost colourless. The yellow form is the one stable at temperatures near its melting point (180°), the colourless variety being transformed into the yellow form without melting before this temperature is reached.

One hundred grams of phthalylphenylhydrazide were melted, and heated slowly in an oil-bath. When the fused mass reached a temperature of about 346°, a vigorous reaction set in, accompanied by the evolution of heat and liberation of nitrogen and ammonia. This temperature was maintained until all action had ceased, when the viscid liquid remaining was distilled. The bulk of it passed over as an orange-yellow liquid, which solidified on cooling to a resin-like solid, a small quantity of coked residue being

left in the distilling flask. The solid distillate was recrystallised from alcohol and glacial acetic acid, and separated in fine, very pale yellow-coloured needles, melting at 208°.

From the mother liquors a small quantity of phthalimide was isolated.

The pale yellow, crystalline product, which formed practically the whole of the distillate, proved to be almost pure phthalanil, the colour being due to a very minute quantity of some yellow-coloured compound, probably a little of the original hydrazide which had escaped decomposition; this could be removed by boiling an alcoholic solution for a long time with animal charcoal, and repeated recrystallisation. A quantity carefully purified in this way melted sharply at 210°, and was identical in every respect with phthalanil made from phthalic anhydride and aniline, which also, when pure, melts at 210°. (Found, C=75·22; H=4·07; N=6·34; M.W.*= 222·7. Calc., C=75·31; H=4·06; N=6·28 per cent. M.W.=223.)

The amounts of nitrogen and ammonia liberated were estimated by carrying out the decomposition of known quantities of the hydrazide in a current of carbon dioxide and hydrogen respectively; but owing to the time required to complete the decomposition, exact quantitative yields could not be obtained. The results, however, show conclusively that phthalylphenylhydrazide when heated decomposes thus:

$$3C_6H_4{<}^{CO}_{CO}{>}N\cdot NHPh = 3C_6H_4{<}^{CO}_{CO}{>}NPh + N_2 + NH_3.$$

*Decomposition of Phthalyl-*p*-bromophenylhydrazide by Heat.*

A similar reaction to that described above occurs when phthalyl-*p*-bromophenylhydrazide is heated, but owing to auto-reduction which goes on simultaneously, considerable quantities of hydrogen bromide are evolved. On distilling the solid product of the decomposition and recrystallising the distillate from alcohol, *p*-bromophthalanil was obtained, crystallising in fine needles (m. p. 204°), and identical with the compound obtained from phthalic anhydride and *p*-bromoaniline.

Decomposition of the Phthalyltolylhydrazides by Heat.

Only the deep yellow-coloured modifications of phthalyl-*o*- and -*p*-tolylhydrazide have up to the present been prepared, the exact conditions necessary for the deposition of the colourless modifications from solution not having yet been realised.

Phthalyl-*p*-tolylhydrazide behaves on heating exactly as does

* By determining the elevation of the boiling point of acetone.

phthalylphenylhydrazide. Twenty grams were similarly heated, when at about 360° a vigorous reaction set in; heat as before was evolved, whilst nitrogen and ammonia were liberated. The yellow residue obtained when the action had completed itself was recrystallised from alcohol, and *p*-tolylphthalimide was obtained, crystallising in fine needles (m. p. 204°), and identical in every respect with the compound prepared by the interaction of phthalic anhydride and *p*-toluidine. Phthalyl-*o*-tolylhydrazide when heated behaved similarly, nitrogen and ammonia were given off, and *o*-tolylphthalimide could be isolated from the residue, but other subsidiary reactions which have not yet been investigated appeared to take place to a much greater extent than in the case of the para-compound.

Decomposition of Benzaldehydephenylhydrazone by Heat.

Benzaldehydephenylhydrazone (m. p. 156°) was placed in a small flask attached to a series of condensers, and gradually heated in an oil-bath. It commenced to decompose at about 210°, and at a temperature a few degrees higher a vigorous action took place, ammonia, nitrogen, and a liquid smelling strongly of benzene being produced. The liquid residue in the flask was heated until gas was no longer given off. The amounts of nitrogen and ammonia produced from weighed quantities of the hydrazone were determined by carrying out the decompositions in a current of carbon dioxide or of hydrogen. The liquid distillate was fractionated, and found to consist of benzene mixed with a very little toluene. The residue after all gas evolution had ceased was fractionally distilled in a vacuum. The lower fractions on cooling solidified to a white, crystalline mass, which on recrystallising from alcohol proved to be stilbene. It crystallised in white, glistening plates, which melted at 124°, and had the peculiar characteristic odour of the hydrocarbon. To complete the identification it was converted into the dibromide, which melted at 237°.

The fractions of higher boiling point which only slowly solidified proved to be benzylideneaniline, $C_6H_5\cdot CH\colon N\cdot C_6H_5$.

Benzaldehydephenylhydrazone, therefore, when heated decomposes in two different ways. In one decomposition, stilbene, nitrogen, and benzene are produced, thus:

$$2CHPh\colon N\cdot NHPh = CHPh\colon CHPh + 2N_2 + 2C_6H_6,$$

a reaction recalling the behaviour of benzylideneazine when heated.

In the other, benzylideneaniline, nitrogen, and ammonia are formed, thus:

$$3CHPh\colon N\cdot NHPh = 3CHPh\colon NPh + N_2 + NH_3,$$

a reaction similar to that which the phthalylhydrazides undergo

when heated. The greater part of the benzaldehydephenylhydrazone decomposes in the latter manner.

The small amount of toluene found is, without doubt, formed by the reduction of the benzylidene group by the hydrazine group, a little diphenyl, which could not be recognised in presence of the stilbene, being possibly also produced.

Decomposition of Benzaldehydetolylhydrazones by Heat.

Benzaldehyde-*p*-tolylhydrazone melts at 120° to a red liquid, which at about 190° decomposes, with evolution of heat, nitrogen, ammonia, and a small amount of toluene being liberated. After the evolution of gas has ceased, if the residual liquid is distilled, a yellow, viscid, oily substance passes over, which on cooling deposits crystals of stilbene. The oily liquid which can be filtered from them is benzylidene-*p*-toluidine, and yields benzaldehyde and *p*-toluidine when hydrolysed by dilute sulphuric acid.

Benzaldehyde-*p*-tolylhydrazone therefore decomposes in a precisely similar manner to benzaldehydephenylhydrazone when heated. The greater part decomposes into benzylidene-*p*-toluidine, nitrogen, and ammonia, thus:

$$3CHPh{:}N{\cdot}NH{\cdot}C_6H_4Me = 3CHPh{:}N{\cdot}C_6H_4Me + N_2 + NH_3,$$

while a considerable but smaller fraction yields stilbene, nitrogen, and toluene, thus:

$$2CHPh{:}N{\cdot}NH{\cdot}C_6H_4Me = CHPh{:}CHPh + 2N_2 + 2C_6H_5Me.$$

Benzaldehyde-*o*-tolylhydrazone decomposes similarly when heated.

UNIVERSITY CHEMICAL LABORATORY,
OXFORD.

CCXXI.—*The Absorption Spectra of Triketohydrindene Hydrate and Certain Derivatives.*

By JOHN EDWARD PURVIS.

THE absorption spectra of a series of coloured diketopyrrolines have been described and discussed by the author (Trans., 1910, **97**, 2535), and also of some derivatives and isomerides of 1 : 2-diketo-Δ^3-*cyclo*pentene (this vol., p. 107).

A series of coloured substances has been described by Ruhemann (Trans., 1910, **97**, 1438; this vol., p. 1486), and obtained from triketohydrindene hydrate, $C_6H_4{<}{\substack{CO\\CO}}{>}C(OH)_2$, which from its

chemical behaviour was found to resemble alloxan very closely. These substances have been studied spectroscopically by the author in order to see how far the colour and absorption is connected (1) with the ketonic constitution, and (2) how far the colour and absorption are modified when the oxygen of the ketonic groups is replaced by other radicle groups. From chemical considerations, Ruhemann ascribed the following constitutional formulæ to the various compounds:

A. Triketohydrindene hydrate, $C_6H_4{<}\substack{CO\\CO}{>}C(OH)_2$, colourless.

B. Diphenylhydrazone of triketohydrindene, $\begin{array}{l} C_6H_4{\cdot}C{:}N{\cdot}NHPh \\ CO\text{---}C{:}N{\cdot}NHPh \end{array}$, red.

C. The hydrate of 2:3-bis-(*p*-dimethylaminoanilo)-*a*-hydrindone, $\begin{array}{l} C_6H_4{\cdot}C{:}N{\cdot}C_6H_4{\cdot}NMe_2 \\ CO\text{---}C{:}N{\cdot}C_6H_4{\cdot}NMe_2 \end{array}$, H_2O, very dark purple.

D. Ketohydrindenophenazine, $\begin{array}{l} C_6H_4{\cdot}C{:}N \\ CO\text{---}C{:}N \end{array}{>}C_6H_4$, canary-yellow.

E. 2-o-Carboxybenzoylindonoglyoxaline,

$$\begin{array}{l} C_6H_4{\cdot}C{\cdot}NH \\ CO\text{---}C\text{---}N \end{array}{\geqslant}C{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H,$$

carmine-red.

F. 1:3-Diketohydrindamine, $C_6H_4{<}\substack{CO\\CO}{>}CH{\cdot}NH_2$, yellow; this substance was not obtained very pure, as it rapidly decomposed.

G. 1:3-Diketo-2-benzylidenehydrindamine,

$$C_6H_4{<}\substack{CO\\CO}{>}CH{\cdot}N{:}CHPh,$$

dull orange.

H. 1:3-Diketo-2-anisylidenehydrindamine,

$$C_6H_4{<}\substack{CO\\CO}{>}CH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OMe,$$

vermilion-orange.

I. 1:3-Diketo-2-*p*-dimethylaminobenzylidenehydrindamine,

$$C_6H_4{<}\substack{CO\\CO}{>}CH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}NMe_2,$$

maroon or very dark red.

K. Diketohydrindylidenediketohydrindamine,

$$C_6H_4{<}\substack{CO\\CO}{>}CH{\cdot}N{:}C{<}\substack{CO\\CO}{>}C_6H_4,$$

deep red.

L. The ammonium salt of *K*,

$$C_6H_4{<}\substack{\text{---}CO\text{---}\\C(ONH_4)}{\geqslant}C{\cdot}N{:}C{<}\substack{CO\\CO}{>}C_6H_4,$$

deep red.

The substances *A*, *B*, *C*, *D*, and *E* were stable in absolute alcohol, although they differed greatly in their relative solubilities. The substances *G*, *H*, *I*, *K*, and *L* were very unstable in alcohol, but they were more stable in glacial acetic acid, and they were investigated when dissolved in that acid. The substance *F* decomposes so rapidly that no observations could be taken. Solutions of the various substances in milligram-molecules by weight were dissolved either in cold absolute alcohol or in glacial acetic acid, and their absorption spectra were examined photographically in the usual way, using Wratten and Wainwright's pan-chromatic plates. For example, $M/100$-solution means that one milligram-molecule by weight of the substance was dissolved in 100 c.c. of cold absolute alcohol or of glacial acetic acid, and this was further diluted so that 1000 c.c. contained one milligram-molecule by weight or $M/1000$-strength; and this again was diluted, so that it became $M/10,000$-strength. The absorption curves of the various solutions have been drawn. It will be seen that the colourless compound *A* has a well-marked band in $M/100$-solution (Fig. 1), the position of which is near the more refrangible end of the visible spectrum. The head of this band is at about 2800 (oscillation frequencies). $M/1000$-Solutions were also examined, but no other band was observed. The positions, the general absorption of which began through the following thicknesses of $M/1000$-solutions, were:

	λ.	$1/\lambda$.
3 mm. thickness	2480	4031
10 ,, ,,	2655	3765
30 ,, ,,	2775	3603
60 ,, ,,	2995	3338

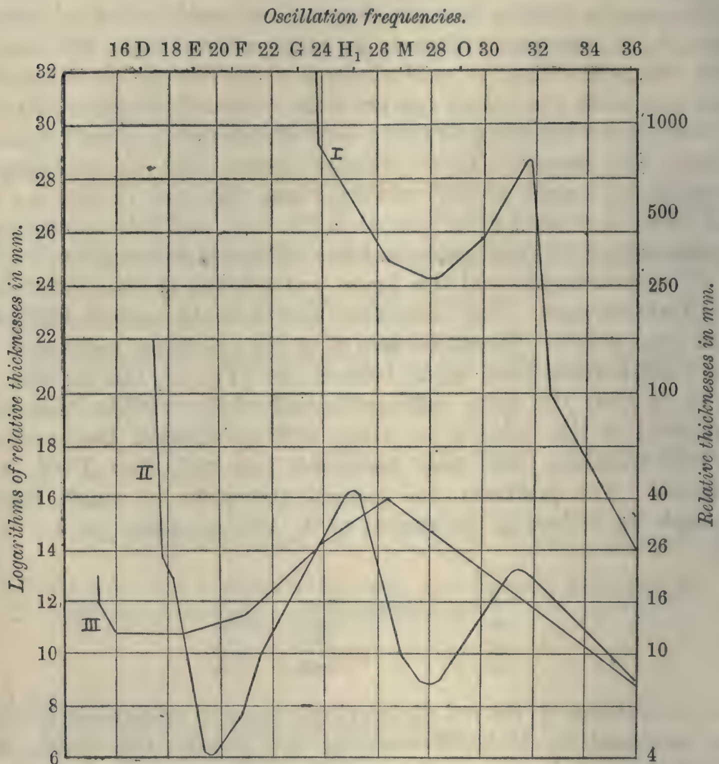
The substance *B*, the red diphenylhydrazone of triketohydrindene, was examined in $M/10,000$-solution, and showed two bands, the curves of which have been drawn (Fig. 1, II). The heads of these two bands are at 2800 and 1980. The more refrangible band, 2800, corresponds with the band found in triketohydrindene.

The substance *C*, a very dark purple, almost black, compound, which gives a very dark purple solution, was also investigated in a $M/10,000$-solution. When examined through a thickness of 24 mm. the solution was so dark that little or no light passed through. It will be seen from the curve (Fig. 1, III) that the two bands of the *B* compound have been fused into one large, not very persistent band, the head of which is at about 1900.

The general effect, therefore, of the substitution of the oxygen of two of the ketonic groups of the colourless compound *A* by complex aromatic nitrogen compounds is to damp the vibrations so that there is absorption of light within the visible regions of the

spectrum, and a characteristic colour is produced. The substances D and E were also examined, but in neither case was a band observed. The positions when general absorption began through

FIG. 1.



I. *Alcoholic solution of triketohydrindene hydrate* (A).
II. ,, ,, *diphenylhydrazone of triketohydrindene hydrate* (B).
III. ,, ,, *the hydrate of* 2 : 3-*bis*-(p-*dimethylaminoanilo*)-α-*hydrindone* (C).

the following thicknesses of M/10,000-alcoholic solutions of the substance D were:

	λ.	1/λ.
9 mm. thickness	3080	3244
30 ,, ,,	3300	3028
51 ,, ,,	3510	2848
90 ,, ,,	3930	2543
135 ,, ,,	4200	2380

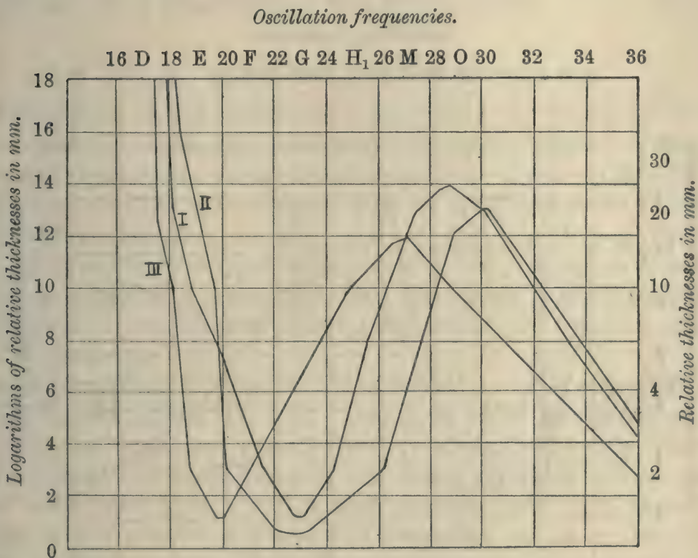
The positions when general absorption began through the following thicknesses of M/10,000-alcoholic solution of the substance E were:

	λ.	1/λ.
9 mm. thickness	2780	3595
30 ,, ,,	3580	2791
51 ,, ,,	3780	2644
90 ,, ,,	3880	2576
134 ,, ,,	4125	2433
146 ,, ,,	4150	2409

Stronger solutions of *D* and *E* were not obtained, as the substances were not easily soluble.

The explanation of these phenomena appears to be that the

FIG. 2.



I. *Acetic acid solution of* 1 : 3-*diketo-2-benzylidenehydrindamine* (G).
II. ,, ,, 1 : 3-*diketo-2-anisylidenehydrindamine* (H).
III. ,, ,, 1 : 3-*diketo-2-*p-*dimethylaminobenzylidenehydrindamine* (I).

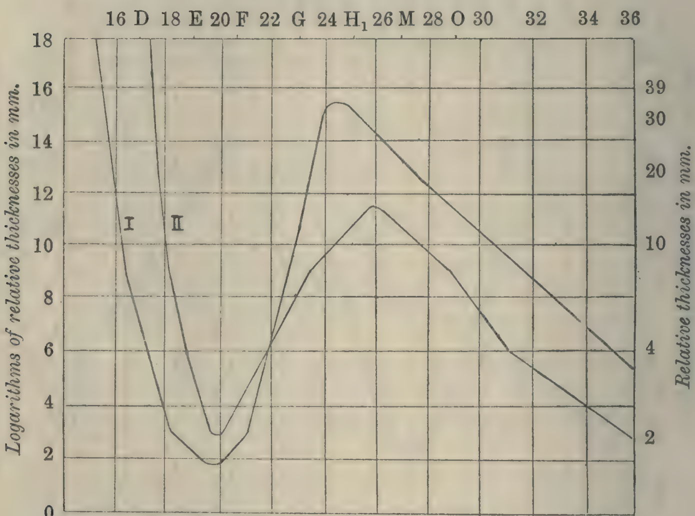
establishment of another ring in each of these compounds has destroyed the selective absorption exhibited by the compounds *A*, *B*, and *C*, and that the colour is produced by an extension of the general absorption within the regions of the visible parts of the spectrum.

The coloured compounds *G*, *H*, and *I* were examined in *M*/1000-solutions of glacial acetic acid, and the absorption curve of the band of each substance has been drawn (Fig. 2). It is evident from a study of these curves that the bands are all of the same type. The differences correspond with differences in the

shades of colour of the different compounds. For example, the substance *G* is a dull orange colour; the substance *H* a vermilion-orange; and the substance *I* is a maroon or a very dark red. The position of the bands, as well as their extension, illustrates these differences in shades of colour. The head of the band *G* is at about 2300; that of *H* is at about 2300, but is much wider than *G*; and that of *I* is about 2000. *M*/10,000-Solutions in glacial acetic acid were also examined through varying thicknesses, but no bands were observed in the ultra-violet regions.

FIG. 3.

Oscillation frequencies.



I. *Acetic acid solution of diketohydrindylidenediketohydrindamine* (K).
II. ,, ,, *the ammonium salt of diketohydrindylidenediketohydrindamine* (L).

The substances *K* and *L* were also examined in *M*/1000-solutions of glacial acetic acid, and the absorption curve of each has been drawn (Fig. 3). Here, again, the bands are evidently of the same type, and the differences correspond with differences in the shades of colour, which are both dark purple-brown. The curve of the ammonium compound (*L*) is not so persistent as that of the parent substance (*K*). The head of the band of *K* is at about 1990, and that of *L* at about 2000. *M*/10,000-Solutions in acetic acid were also examined through varying thicknesses, but no bands were

observed in the ultra-violet regions. The positions where general absorption began in $M/10,000$-solutions were:

		λ.	$1/\lambda$.
K.	10 mm. thickness	2810	3556
	2 ,, ,,	2490	4014
L.	10 ,, ,,	2700	3702
	2 ,, ,,	2465	4054

So that the general effect of the substitution of oxygen in one of the ketonic groups of the colourless compound *A*, by complex aromatic compounds, is to damp the vibrations so that there is a selective absorption of light within the visible regions of the spectrum, and a characteristic colour is produced.

General Conclusions.

The results of the observations show that (1) the colour of the compounds is intimately connected with the presence of ketonic groups, phenomena which are analogous to those of the diketopyrrolines and the *cyclo*pentenes (*loc. cit.*); (2) the shade of colour is modified according to the type of the substituting groups; (3) where another ring is established, as in the compounds *D* and *E*, there is no selective absorption, and the colour is produced by an extension of the general absorption within the regions of the visible spectrum.

It is important to refer to the observations of Hartley (Trans., 1887, **51**, 154; 1905, **87**, 1791 *et seq.*), in which he shows that the colourless alloxan and uramil have no absorption bands, whereas the coloured murexide has two, the heads of which are at about 3300 and 1900; that is, the former, a weak band, is in the ultraviolet, and the latter, a strong and persistent one, is in the visible parts of the spectrum. These three compounds are constitutionally comparable with the compounds *A*, *F*, and *L* respectively. The comparison may be further extended in that the parent substance *A* (triketohydrindene hydrate) has no colour, although it exhibits an absorption band just beyond the visible part of the spectrum; the unstable substance *F* (1:3-diketohydrindamine) would probably show a similar band; and the coloured substance *L* (the ammonium salt of diketohydrindylidenediketohydrindamine) exhibits a band in the visible regions of the spectrum.

Apart from this comparison, it is also clear that selective absorption need not accompany the phenomenon of colour, as the author has shown in the isomerides of *cyclo*pentene (*loc. cit.*); and the observation is confirmed by the coloured compounds *D* and *E* of this investigation, where no selective absorption was found.

Although there is no selective absorption, it is probable that the colour is the result of the transmission of rays between definite regions, the limit of which, in one direction, extends into the infra-red; and there is every possibility that such compounds would show selective absorption in these regions.

I have again to thank the Government Grant Committee of the Royal Society, by whose assistance the spectroscope was obtained; and also Dr. Ruhemann for pure specimens of the substances examined.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CCXXII.—*The Alkaline Condensations of Nitro-hydrazo-compounds. Part I.*

By ARTHUR GEORGE GREEN and ERNEST ARTHUR BEARDER.

IN a series of researches on the constitution of the stilbene dyestuffs conducted by Green and former collaborators (Trans., 1904, **85**, 1424, 1432; 1906, **89**, 1602; 1907, **91**, 2076; 1908, **93**, 1721), it has been shown that the production of azostilbene compounds, whether by alkaline condensation of derivatives of *p*-nitrotoluene or by alkaline reduction of derivatives of 4:4′-dinitrostilbene, is preceded by the formation of unstable intermediate products, to which the constitution of nitrosostilbenes was assigned.

In view of the parallelism between the $\cdot N\colon N\cdot$ and $\cdot CH\colon CH\cdot$ series which is exhibited in the following, amongst other, reactions:

$$\underset{p\text{-Nitrotoluene.}}{H_3C\cdot C_6H_4\cdot NO_2} \xrightarrow[\text{hypochlorites}]{\text{Oxidation with}} \underset{4:4'\text{-Dinitrostilbene.}}{NO_2\cdot C_6H_4\cdot CH\colon CH\cdot C_6H_4\cdot NO_2}$$

$$\underset{p\text{-Nitroaniline.}}{H_2N\cdot C_6H_4\cdot NO_2} \xrightarrow[\text{hypochlorites}]{\text{Oxidation with}} \underset{4:4'\text{-Dinitroazobenzene.}}{NO_2\cdot C_6H_4\cdot N\colon N\cdot C_6H_4\cdot NO_2}$$

it seemed not improbable that condensations might occur in the azo-series similar to those which give rise to the stilbene dyestuffs. It has long been known that by partial reduction of 4:4′-dinitroazobenzene a product is obtained which dissolves in alkali hydroxides with an intense blue colour, and it appeared possible that an analogy might exist between this product and the above-mentioned intermediate compounds of the stilbene class, which dissolve in alkalis with a crimson to blue colour. This anticipation was strengthened when we found that the former substance exhibited

in its general behaviour a remarkable similarity to the latter class of compounds. Thus, in alkaline solution both are readily decolorised by air, the former yielding dinitroazobenzene, the latter dinitrostilbene. On heating their alkaline solutions, both are finally converted into stable yellow condensation products, which dissolve in concentrated sulphuric acid with a similar cherry-red colour. Further, in both cases these stable condensation products are converted by alkaline reducing agents into other products dissolving in concentrated sulphuric acid with a blue colour.

Assuming that the intermediate products of the stilbene condensation are correctly regarded as nitroso-compounds, the existence of a series of parallel condensations in the azo-class would necessitate the conclusion, either that the above reduction product of dinitroazobenzene, which is usually regarded as dinitrohydrazobenzene, is actually a nitroso-compound, or that such a nitroso-compound is formed in an early stage of its alkaline condensation. The present research has been undertaken with the object of investigating these questions, and, incidentally, of obtaining further light on the course of the stilbene reactions.

The product of the partial reduction of 4:4′-dinitroazobenzene, which dissolves with a bright blue colour in aqueous alkalis, has already been the subject of frequent investigations, which have led to very divergent views as to its constitution. It was discovered by Lermontoff in 1872 (*Ber.*, 1872, **5**, 232), who regarded it as a dinitrohydrazobenzene, $N_2H_2(C_6H_4{\cdot}NO_2)_2$, a conclusion which was strongly supported later by the work of Werner and Stiasny (*Ber.*, 1899, **32**, 3272). On the other hand, Janovsky (*Monatsh.*, 1885, **6**, 160), whose analytical results differ widely from those of other authors, ascribes to the compound the constitution of a nitrolic acid, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N(OH){\cdot}N(OH){\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2$. Willgerodt (*J. pr. Chem.*, 1890, [ii], **42**, 51) regards it as an "az-hydroxyazo" compound, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NH(OH){:}O$; whilst Freundler and Beranger (*Compt. rend.*, 1902, **134**, 1219) support the quinonoid formula: $HO_2N{:}C_6H_4{:}N{\cdot}N{:}C_6H_4{:}NO_2H$. Another possible structure hitherto unconsidered is that of a hydrated dinitrosoazobenzene, $(HO)_2N{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N(OH)_2$.

The preparation of this product at first offered some difficulties, owing to the absence of details in the published accounts, but it was finally obtained in a pure state and in good yield by reduction with colourless ammonium sulphide. When crystallised from acetone it had the characteristic crystalline form described by Janovsky, and after drying at 140° it melted (if heated quickly) at 228°, as given by Werner and Stiasny. The great variation in melting point observed by different investigators (L., 220°; J., 218°;

W., 248—250°; W. and S., 228°), which at first sight seems to suggest that they had varying products in hand, is more probably to be referred to the different rate of heating. The nitrogen value obtained for the compound agreed exactly with a dinitrohydrazobenzene, although it also approximated to the figure required for the hydrated dinitrosoazobenzene. On oxidising the blue alkaline solution by shaking with air or by addition of iodine, dinitroazobenzene was regenerated. Titration of the alkaline solution with a standard solution of iodine until complete disappearance of the blue colour, gave results which indicated the removal of two atoms of hydrogen. Titration of the acetic acid solution with titanium trichloride also gave figures in agreement with the dinitrohydrazobenzene formula, and this was further supported by the behaviour of the compound with acetic anhydride. When heated with this reagent for a short time only it remained unaltered, whereas if it were a hydrated form of dinitrosoazobenzene, or had the "azhydroxyazo" formula suggested by Willgerodt, it should lose the elements of water. When boiled with a large excess of acetic anhydride for two hours it was converted into a diacetyl derivative, melting at 188—189°, which is doubtless identical with the dinitrodiacetylhydrazobenzene (m. p. 186—187°) obtained by Freundler and Beranger by nitration of diacetylhydrazobenzene. There is thus no reason to doubt the correctness of the conclusion arrived at by Werner and Stiasny, that the reduction product is actually dinitrohydrazobenzene.

The question next arises whether the blue colour of the alkaline solution is due to the formation of a salt of dinitrohydrazobenzene or whether a molecular change occurs under the influence of the alkali.

To ascertain this, a series of experiments was conducted, in which weighed quantities of the dinitrohydrazobenzene were dissolved in cold aqueous sodium hydroxide (10 to 20 per cent. NaOH), and then filtered into aqueous acid, both solution and filtration being effected in an apparatus from which air was completely excluded by means of hydrogen. If intermolecular oxidation and reduction occurred, it was to be expected that a precipitate of dinitroazobenzene would be produced. The dinitrohydrazobenzene dissolved completely, and the deep blue liquid, when not allowed to remain for more than fifteen minutes, left no appreciable precipitate on the filter. We further found that the freshly prepared blue solution gave when immediately acidified a light yellow precipitate of unaltered dinitrohydrazobenzene. It must therefore be concluded that the blue compound actually represents an alkali salt of dinitrohydrazobenzene, and if its entirely different colour and

much greater oxidisability in comparison with the free compound be considered, the assumption seems justified that the latter is a pseudo-acid, giving rise to salts of the quinonoid type,

$$M'O\cdot ON:C_6H_4:N\cdot N:C_6H_4:NO\cdot OM'.$$

This conclusion is also in agreement with the work of Grandmougin and Leeman (*Ber.*, 1906, **39**, 4384; 1908, **41**, 1295), who have isolated a blue dipotassium salt of hexanitrohydrazobenzene,

$$C_6H_2(NO_2)_3\cdot NH\cdot NH\cdot C_6H_2(NO_2)_3.$$

In the course of the above experiments it was observed that if the blue solution in aqueous sodium hydroxide (10 per cent. NaOH) is kept with exclusion of air for several hours, the colour becomes slightly more violet, whilst a small precipitation of dinitroazobenzene occurs. If the blue solution is now acidified, the precipitate has a much more orange colour than previously, is more voluminous, and is completely soluble in cold glacial acetic acid, in which dinitrohydrazobenzene scarcely dissolves at all. It also exhibits a much greater solubility in alcohol and in ether. In aqueous sodium hydroxide it dissolves readily with the same blue colour as dinitrohydrazobenzene, but, on the other hand, dissolves in sulphuric acid with a reddish-orange colour, in contrast to the pure yellow of the latter. When dry it forms a brick-red, amorphous powder, which could not be obtained crystalline. Analysis of this product gave numbers for carbon, hydrogen, and nitrogen conforming to dinitrohydrazobenzene, with which the results of titration with titanium trichloride were also in correspondence. If boiled, however, with acetic anhydride under conditions in which dinitrohydrazobenzene is quantitatively converted into the diacetyl derivative, the product in question gave rise to dinitroazobenzene (yield of about 70 per cent.). These results appeared at first sight to indicate that we had in hand a compound isomeric with the original dinitrohydrazobenzene. Such a supposition was, however, very difficult to express by any probable formula, and doubts arose as to its validity when it was found possible by repeated crystallisation from acetone to separate from the product a small quantity of pure dinitrohydrazobenzene. Subsequent experiments proved that the substance was in fact a mixture consisting of about four-fifths of unaltered dinitrohydrazobenzene with about one-fifth of a new compound. The latter was obtained pure by effecting the conversion with weaker alkali (3 per cent. NaOH), and allowing the solution to remain at the summer temperature (about 25°) for from six to sixteen hours. A violet-blue solution was thus produced, in which was suspended a considerable amount of dinitroazobenzene. After filtration from the latter the blue solution was acidified with acetic acid, which produced a very voluminous, colloidal, orange-red

precipitate. By rapid crystallisation from acetone the new compound was obtained in small, red cubes with a violet reflex. In concentrated sulphuric acid it dissolved with a pure crimson colour, which on addition of a drop of dilute nitric acid was changed to yellow (formation of dinitroazobenzene). It dissolved in alkali hydroxides to a violet-blue solution, which, like that of dinitrohydrazobenzene, is decolorised by air or iodine. A determination of the relative quantities of the new compound and of dinitroazobenzene produced from a given weight of dinitrohydrazobenzene gave results in agreement with the supposition that the reaction proceeds according to one or other of the two following equations:

(*a*) $2NO_2 \cdot C_6H_4 \cdot N_2H_2 \cdot C_6H_4 \cdot NO_2 =$

$$NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NO_2 + C_{12}H_{10}O_3N_4 + H_2O.$$

(*b*) $2NO_2 \cdot C_6H_4 \cdot N_2H_2 \cdot C_6H_4 \cdot NO_2 =$

$$NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NO_2 + C_{12}H_8O_2N_4 + 2H_2O.$$

The estimation of carbon, hydrogen, and nitrogen, and the results obtained by titration with titanium trichloride, establish for the compound the constitution $C_{12}H_{10}O_3N_4$; it is therefore formed in accordance with the first equation. The substance is therefore either a 4-nitro-4′-nitrosohydrazobenzene,

$$NO \cdot C_6H_4 \cdot NH \cdot NH \cdot C_6H_4 \cdot NO_2,$$

or a hydrated 4:4′-dinitrosoazobenzene,

$$NO \cdot C_6H_4 \cdot N{:}N \cdot C_6H_4 \cdot N(OH)_2.$$

As, however, the titration of the alkaline solution with standard iodine indicates the loss of two atoms of hydrogen in a similar manner to dinitrohydrazobenzene, the first of these formulæ appears the more probable.

Accepting the conclusion that the free compound is nitronitrosohydrazobenzene, it is probable that its violet-blue alkaline solutions contain quinonoid salts of the constitution

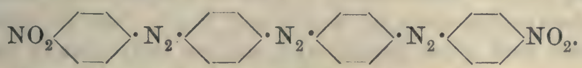
$$M'O \cdot ON{:}C_6H_4{:}N \cdot N{:}C_6H_4{:}N \cdot OH.$$

These salts should be identical with the oxime corresponding with the red alkaline salts of *p*-nitrobenzeneazophenol, to which Hewitt assigns the formula $M'O \cdot ON{:}C_6H_4{:}N \cdot N{:}C_6H_4{:}O$. Attempts to prepare the former by the action of hydroxylamine on the latter have not, however, been successful.

In respect to the incomplete action of cold alkali hydroxides on dinitrohydrazobenzene, it was found by direct experiment that a mixture composed of one part of nitronitrosohydrazobenzene and four parts of dinitrohydrazobenzene, when precipitated together, exhibited exactly the same properties as the product at first supposed to be an isomeric dinitrohydrazobenzene. The orange colour in sulphuric acid, its colloidal properties, and much greater solubility in solvents are therefore all due to the admixture of

nitronitrosohydrazobenzene. The different behaviour of the product with acetic anhydride appears also to be referable to the same cause, for the nitroso-compound on account of its greater reducibility may effect oxidation of dinitrohydrazobenzene to dinitroazobenzene before acetylation can occur.

As mentioned above, the final product of the action of alkali hydroxides on dinitrohydrazobenzene is very analogous to the final product of the stilbene condensation. It was obtained by heating the solution of nitronitrosohydrazobenzene in 3 per cent. sodium hydroxide to 100° until complete disappearance of the blue colour (air being rigidly excluded). The orange-coloured precipitate, after crystallisation from xylene, was obtained in sparingly soluble, orange needles, melting at 285—286°. Analysis supported the constitution:



The compound is therefore a *bisnitrobenzeneazo-azobenzene*, and owes its formation to the condensation of two molecules of nitronitrosohydrazobenzene, in accordance with the scheme:

$$NO_2\cdot C_6H_4\cdot \overset{H}{N}\cdot \overset{H}{N}\cdot C_6H_4\cdot \overset{O}{N} \longrightarrow \longleftarrow \overset{O}{N}\cdot C_6H_4\cdot \overset{H}{N}\cdot \overset{H}{N}\cdot C_6H_4\cdot NO_2$$

In preparing the compound it is not necessary to employ the isolated nitronitrosohydrazobenzene, but the blue alkaline solution of dinitrohydrazobenzene may be heated at once to 100° until the blue colour disappears. The orange precipitate then obtained is a mixture of bisnitrobenzeneazo-azobenzene with dinitroazobenzene, and can be readily separated by solvents, in which the former compound is much less soluble. A quantitative determination of the yield of the two products agreed with the equation:

$$4NO_2\cdot C_6H_4\cdot N_2H_2\cdot C_6H_4\cdot NO_2 = 2NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NO_2 + C_{24}H_{16}O_4N_8 + 4H_2O.$$

It was further found that the condensation of nitronitrosohydrazobenzene to bisnitrobenzeneazo-azobenzene can also be effected by merely boiling the former with neutral solvents.

The above experiments fully justify our original expectation of the existence of a parallelism between the derivatives of dinitroazobenzene and those of dinitrostilbene. If this analogy is complete it would seem to suggest that the intermediate products of the stilbene reaction are not, as hitherto believed, dinitrosostilbenes, $NO\cdot C_6H_4\cdot CH\colon CH\cdot C_6H_4\cdot NO$, but rather nitronitrosodibenzyls,

$$NO\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

from which the final condensation products (stilbene dyestuffs) are formed in the manner indicated above for bisnitrobenzeneazo-azo-

benzene. The mobility of the two methylene hydrogen atoms may very probably be connected with the tendency to form quinonoid salts. The chief difficulty in this view lies in the fact that coloured (blue?) quinonoid salts of dinitrodibenzyl,

$$M'O{\cdot}ON{:}C_6H_4{:}CH{\cdot}CH{:}C_6H_4{:}NO{\cdot}OM',$$

corresponding with the blue quinonoid salts of dinitrohydrazobenzene, have hitherto not been observed. The dinitrodibenzyl salts and those of its derivatives which have been investigated all give no colour with alkali hydroxides, except on heating. It is, however, possible that owing to the firmer attachment of hydrogen to carbon compared with that of hydrogen to nitrogen, the formation of quinonoid salts may take place with greater difficulty, or only at temperatures at which conversion into the nitronitroso-compound follows immediately. This is supported to some extent by the observation made by Green and Wahl, that dinitrodibenzyl-disulphonic acid when heated with sodium hydroxide is converted, in the first instance, into a mixture of dinitrostilbenedisulphonic acid with the crimson intermediate product. If the latter is nitronitrosodibenzyldisulphonic acid, the reaction is exactly analogous to the above-described formation of dinitroazobenzene and nitronitrosohydrazobenzene from two molecular proportions of dinitrohydrazobenzene, and just as in this case may be preceded and conditioned by the prior formation of a quinonoid salt.

Experimental.

4:4′-*Dinitroazobenzene.*

This compound was prepared both by nitration of azobenzene and by oxidation of *p*-nitroaniline with calcium hypochlorite, identical products being obtained in both cases. The latter method, by which the pure product can readily be obtained in quantity, was that finally adopted. In conformity with Meigen and Normann (*Ber.*, 1900, **33**, 2711), we found that the product of this reaction is the azo- and not the azoxy-compound. The operation is best conducted in the following manner: One hundred grams of *p*-nitroaniline are dissolved in a mixture of hydrochloric acid and hot water, filtered through glass wool, and poured into about 2½ litres of cold water, the base being thus obtained in a fine state of division. The mixture is then rendered alkaline with sodium hydroxide, and a clear solution of calcium hypochlorite added, containing about 50 per cent. more chlorine than that theoretically required. After stirring for about six hours and leaving overnight, the orange precipitate is collected, washed well with cold water, and then without drying extracted on the filter with cold acetone,

in order to remove unaltered *p*-nitroaniline and dark-coloured by-products. The residue is recrystallised from boiling xylene, from which it separates in long, orange-red leaflets, melting at 222—223°. To facilitate the subsequent reduction, it was found very advantageous to convert the product into a fine state of division by dissolving it in cold concentrated sulphuric acid, and pouring into water. In this case it is not necessary to crystallise from xylene, and the purification with acetone may be conveniently replaced by an extraction with cold dilute hydrochloric acid to remove *p*-nitroaniline, calcium carbonate, and other impurities. (Found, N = 20·87. Calc., N = 20·59 per cent.)

4 : 4′-*Dinitrohydrazobenzene*, $NO_2 \cdot C_6H_4 \cdot NH \cdot NH \cdot C_6H_4 \cdot NO_2$.

After a number of experiments with various alkaline reducing agents, such as zinc dust and sodium hydroxide, dextrose and alkali, sodium sulphide, yellow ammonium sulphide, etc., none of which gave good results, the following method of preparation with colourless ammonium sulphide was adopted. The reagent was prepared just before use by saturating a mixture of equal parts of concentrated aqueous ammonia and water with hydrogen sulphide. Eleven grams of finely divided dinitroazobenzene are mixed in a mortar to a uniform paste with 150 c.c. of 95 per cent. alcohol, to which a few c.c. of acetone are added. The paste is transferred to a flask, heated to boiling, and 100 c.c. of the above aqueous ammonium sulphide are brought in. An immediate reaction occurs, and after about two minutes' boiling an equal volume of cold water is added. After cooling, the yellow precipitate is collected, washed with hot water, and then with alcohol, after which it is extracted with chloroform to remove any sulphur that may be present. The product is then dissolved in about 300 c.c. of boiling acetone (to which a little alcohol is added), and on cooling dinitrohydrazobenzene separates in pale yellow, transparent, rhombic prisms. The product on drying at 140° loses acetone, becoming opaque and of a deeper yellow colour. The yield was 6 or 7 grams. The product dried at 140° was found to melt at 228° if heated quickly, but on slower heating it melted at various other temperatures up to 250°. (Found, N = 20·4. Calc., N = 20·4 per cent.)

Reduction in acetic acid solution with standard titanium trichloride, titrating back the excess with ferric alum, gave the following result:

Hydrogen used = 5·08, 5·27, 5·17.

Hydrogen theoretically necessary for reduction of dinitrohydrazobenzene to *p*-phenylenediamine = 5·11 per cent.

In order to estimate the quantity of oxygen required to effect

decolorisation of the alkaline solution, titration with standard iodine in an atmosphere of hydrogen was employed. The end-point, indicated by the disappearance of the blue colour, is sharply defined. To secure rapid solution of the dinitrohydrazobenzene in the dilute sodium hydroxide employed and thus avoid any condensation, it was found advisable previously to dissolve the compound in acetone, reprecipitate with water, and wash thoroughly until every trace of acetone was removed. The fine precipitate was then transferred to a closed flask with 50 c.c. of water, the air displaced by hydrogen, and 50 c.c. of 6 per cent. sodium hydroxide were introduced from a tap funnel. Titration is then effected with $N/20$-iodine immediately solution has occurred:

Oxygen consumed = 6·3 and 5·96.

Oxygen required to oxidise dinitrohydrazobenzene to dinitroazobenzene = 5·79 per cent.

Dinitrodiacetylhydrazobenzene, $NO_2 \cdot C_6H_4 \cdot NAc \cdot NAc \cdot C_6H_4 \cdot NO_2$.

One gram of dinitrohydrazobenzene was boiled for two hours with 20 c.c. of acetic anhydride, air being excluded. After evaporating off the excess of acetic anhydride, the mass was extracted with cold chloroform, and the residue crystallised from boiling glacial acetic acid. The product separated in colourless plates, which melted at 188—189°. It was insoluble in cold alkali hydroxides, but on boiling gave the deep blue colour of dinitrohydrazobenzene. (Found, N = 15·81. Calc., N = 15·64 per cent.)

4 : 4′-*Nitronitrosohydrazobenzene*, $NO \cdot C_6H_4 \cdot NH \cdot NH \cdot C_6H_4 \cdot NO_2$.

This compound constitutes the first stage of the action of alkali hydroxides on dinitrohydrazobenzene. The best conditions for obtaining it in a pure state free from unconverted dinitrohydrazobenzene and from the bisnitrobenzeneazo-azobenzene produced by further condensation were only ascertained after a long series of experiments. Although the condensation commences almost immediately, the rate of the reaction is dependent on the temperature of the solution and its concentration in alkali hydroxide; thus with sodium hydroxide solutions of from 10 to 20 per cent. the reaction is much slower than with solutions of only 3 per cent. With solutions of the former strength and at a temperature of about 15° we obtained colloidal mixtures, in which dinitrohydrazobenzene largely preponderated, but which, nevertheless, exhibited very different properties from the latter in the pure state (see introduction). It was finally ascertained that a complete conversion into

the nitronitroso-compound, without any further condensation, is effected by allowing dinitrohydrazobenzene dissolved in eighty parts of 3 per cent. sodium hydroxide to remain at 25° (laboratory summer temperature) for from six to sixteen hours. The operation is best carried out in a bottle provided with a well-fitting, greased stopper, and nearly filled in order to exclude air. The progress of the reaction can be followed by precipitating at intervals small samples of the filtered solution with acetic acid, and dissolving the precipitate in concentrated sulphuric acid. After only a minute or two the solution in sulphuric acid is pure yellow (unaltered dinitrohydrazobenzene), after ten minutes it is reddish-orange, after half an hour red, and after five hours pure crimson, whilst after sixteen hours no further change is visible. When this point is reached the violet-blue solution is filtered quickly from precipitated dinitroazobenzene, and the filtrate allowed to run directly into an excess of dilute acetic acid. The product was a highly voluminous, gelatinous, reddish-orange precipitate, readily soluble in cold glacial acetic acid, acetone, ether, etc. It was washed thoroughly with water, pressed, dried at the ordinary temperature, and dissolved in acetone. On quickly evaporating the acetone the compound crystallised in small, orange-red cubes with a violet reflex. It is necessary to work quickly in order to avoid condensation of the nitronitroso-compound to bisnitrobenzeneazo-azobenzene. *Nitronitrosohydrazobenzene* is readily soluble in solvents such as acetone, alcohol, ether, acetic acid, but sparingly so in hydrocarbons. The solution in acetone has a deep yellow colour, which was found to be about forty times as intense as a similar solution of dinitrohydrazobenzene. The substance has pronounced tinctorial properties, dyeing silk from an aqueous alcoholic solution in red shades, which are changed to blue by immersion in dilute sodium hydroxide. It has no definite melting point, but begins to decompose at about 203°. Its alkali hydroxide solution has a more violet tint of blue than that of dinitrohydrazobenzene. Like the latter it is decolorised by air or iodine. In addition to its acid properties the compound appears also to be a weak base, giving pink solutions with aqueous acids. It dissolves in concentrated sulphuric acid with a pure crimson colour, which is changed to pure yellow (dinitroazobenzene) on adding a drop of dilute nitric acid.

On account of its instability the compound was analysed in the air-dried condition, the percentage of moisture it contained being determined simultaneously by drying at 140°, and the correction introduced:

0·0967 * gave 0·1990 CO_2 and 0·0348 H_2O. C=56·05; H=3·95.
0·0964 * „ 0·1992 CO_2 „ 0·0367 H_2O. C=56·34; H=4·22.
0·0950 * „ 0·1917 CO_2 „ 0·0355 H_2O. C=55·1; H=4·1.
0·0991 * „ 19·6 c.c. N_2 at 25° and 757·5 mm. N=22·64.
0·1006 * „ 19·9 c.c. N_2 „ 26·5° „ 760·3 mm. N=22·73.
0·0943 * „ 18·3 c.c. N_2 „ 23° „ 754 mm. N=22·73.
Mean: C=55·83; H=4·09; N=22·7.

$C_{12}H_{10}O_3N_4$ requires C=55·67; H=3·91; N=21·7 per cent.

Reduction in a boiling acetic acid solution with a standard solution of titanium trichloride gave the following results:

Hydrogen consumed=5·36 and 5·06.

Hydrogen required for reduction to *p*-phenylenediamine=4·70 per cent.

Titration of the alkaline solution with standard iodine in an atmosphere of hydrogen (in the manner described above, but without previously dissolving in acetone) gave the following results:

Oxygen consumed=5·55 and 5·53.

Oxygen required to oxidise nitronitrosohydrazobenzene to nitronitrosoazobenzene=6·15 per cent.

Attempts to isolate nitronitrosoazobenzene from the orange-yellow precipitate formed in this reaction proved unsuccessful, the nitroso-compound apparently undergoing further condensation in the alkaline medium or during subsequent purification.

The conclusion based on the above analyses, that under the influence of alkali hydroxides two molecular proportions of dinitrohydrazobenzene give rise to one of nitronitrosohydrazobenzene and one of dinitroazobenzene, was further supported by the following quantitative experiments:

A. 3·75 Dinitrohydrazobenzene gave 1·632 nitronitrosohydrazobenzene and 1·879 dinitroazobenzene. The quantities theoretically required are 1·765 of the former and 1·861 of the latter.

B. A solution of 0·0522 dinitrohydrazobenzene in 3 per cent. sodium hydroxide was allowed to remain for five hours at 25°, air being carefully excluded by means of hydrogen. At the end of this time the solution was titrated with standard iodine (in absence of air) until the disappearance of the blue colour.

The iodine required was equivalent to 0·00132 gram of oxygen.

Percentage of oxygen consumed=2·5, that is, approximately half the quantity (5·79) which would have been required had the solution been titrated immediately.

* Dry.

Bisnitrobenzeneazo-azobenzene,
$NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NO_2$.

This substance is readily formed by further condensation of nitronitrosohydrazobenzene, either by heating the alkaline solution or by boiling the substance itself with neutral solvents. In place of employing nitronitrosohydrazobenzene itself, the alkaline solution of dinitrohydrazobenzene may be directly heated, in which case dinitroazobenzene is formed simultaneously.

I. Finely powdered nitronitrosohydrazobenzene was placed in a well-stoppered bottle filled with about fifty parts of aqueous 3 per cent. sodium hydroxide, and heated in boiling water until the blue colour had entirely disappeared, leaving a red liquid, in which was suspended a bright orange precipitate. The time of heating required was about four hours. The orange precipitate was collected, well washed with water, and dried. The crude product was almost pure, and melted at about 285°. It contained no dinitroazobenzene.

II. About 1½ grams of dinitrohydrazobenzene were heated as above with 70 c.c. of aqueous 3 per cent. sodium hydroxide. When the conversion was complete, the precipitate was collected, washed, and dried. It was then boiled with glacial acetic acid, which dissolved about half the whole, and on cooling deposited dinitroazobenzene in the characteristic orange plates, melting at 222·5—223°. The insoluble residue was dissolved in a large volume of boiling solvent-naphtha, from which after filtration and cooling bisnitrobenzeneazo-azobenzene crystallised in very small, brownish-orange needles, melting at 285—286°.

III. 0·1748 Gram of nitronitrosohydrazobenzene was boiled with 50 c.c. of solvent naphtha until it dissolved completely (about six hours' boiling were necessary). The solution was concentrated to about half its volume, and allowed to cool, when the condensation product crystallised out in microscopic, orange-brown needles, which melted at 284—285°. The yield was 0·1042 gram, the conversion being complete.

For analysis the substance was dried at 140°:

0·0923 gave 0·2022 CO_2 and 0·0297 H_2O. C = 59·74; H = 3·57.
0·0863 „ 16·6 c.c. N_2 at 30·5° and 773 mm. N = 22·2.
0·0718 „ 14 c.c. N_2 at 28° and 767 mm. N = 22·5.
$C_{24}H_{16}O_4N_8$ requires C = 60·0; H = 3·33; N = 23·3 per cent.

This constitution is further supported by a determination of the relative quantity of condensation product and dinitroazobenzene produced from a given weight of dinitrohydrazobenzene:

0·9024 dinitrohydrazobenzene gave 0·4531 bisnitrobenzeneazo-azobenzene and 0·4372 dinitroazobenzene. This approximates very closely to that theoretically required.

Bisnitrobenzeneazo-azobenzene crystallises in very small, orange needles or leaflets, and is very sparingly soluble in all solvents. Its concentrated sulphuric acid solution is cherry-red, which becomes more crimson on addition of a small quantity of water, and is not decolorised by a drop of dilute nitric acid (distinction from the nitronitroso-compound). Alkaline reducing agents convert it into a compound which dissolves in concentrated sulphuric acid with a blue colour, and the investigation of which is at present proceeding.

DEPARTMENT OF TINCTORIAL CHEMISTRY,
UNIVERSITY, LEEDS.

CCXXIII.—*Trimercuridiethylammonium Nitrite.*

By PRAFULLA CHANDRA RÂY and JITENDRA NATH RAKSHIT.

IT is well known that when a solution of mercuric chloride is treated with ammonia, the so-called infusible white precipitate is obtained, to which the formula $NHg''H_2Cl$ has been assigned. One of us has shown that the interaction of mercuric nitrite and aqueous ammonia gives rise to dimercuriammonium nitrite, $NHg_2''NO_2$ (Trans., 1902, **81**, 645). This compound may be regarded as ammonium nitrite, in which the four atoms of hydrogen have been displaced by two atoms of dyad mercury. If mercuric chloride is acted on by ethylamine instead of ammonia, the alkyl substituted compound, $NHg''EtHCl$, is, as might be expected, the product of reaction.

We treated a solution of mercuric nitrite with methylamine with a view to ascertain if the formation of a corresponding alkyl derivative takes place. Although we failed to obtain the expected compound, dimercuriammonium nitrite being the product, an examination of the filtrate led to the isolation of methylammonium nitrite (this vol., p. 1016). Reference has already been made to the fact that, by the interaction of ethylamine and mercuric nitrite, not only dimercuriammonium nitrite, but also the alkyl substituted compound, trimercuridiethylammonium nitrite, $N_2Hg_3''Et_2(NO_2)_2$, is obtained (this vol., p. 1470). Ethylammonium nitrite, of course, remains in the filtrate.

Method of Preparation.—To a solution of mercuric-sodium nitrite is added an aqueous solution of ethylamine, taking care that the beaker is vigorously shaken after each addition. The reaction may

be taken as completed when the odour of ethylamine distinctly persists, even after a lapse of several minutes. The flocculent, heavy precipitate is washed by the aid of the pump, and dried in a steam-oven. The substance is perfectly white, whereas dimercuri-ammonium nitrite is pale yellow. In fact, by the physical difference in this property alone the one could be distinguished from the other. By a little practice the conditions which favour the formation of trimercuridiethylammonium nitrite to the exclusion of dimercuriammonium nitrite can be secured. The reaction evidently takes place according to the equations:

$$3\,Hg''(NO_2)_2 + 6NH_3Et{\cdot}OH = N_2Hg_3''Et_2(NO_2)_2 + 4NH_3Et{\cdot}NO_2 + 6H_2O \quad . \; . \; . \quad (1)$$

$$2\,Hg''(NO_2)_2 + 4NH_3Et{\cdot}OH = NHg_2''NO_2 + EtOH + 3NH_3Et{\cdot}NO_2 + 3H_2O \quad . \; . \; . \quad (2)$$

The substance dissolves readily in hydrochloric acid with the evolution of nitrous fumes.

Found: $Hg = 75{\cdot}30,\ 75{\cdot}33$; $C = 6{\cdot}24,\ 6{\cdot}02$; $N = 7{\cdot}30,\ 7{\cdot}72$.

$C_4H_{10}O_4N_4Hg_3,H_2O$ requires $Hg = 75{\cdot}37$; $C = 6{\cdot}03$; $N = 7{\cdot}04$ per cent.

The hydrogen was not estimated owing to the risk of vapour of mercury entering into the calcium chloride tube, and thus vitiating the results. The salt evidently contains one molecule of water of crystallisation; this is quite in accord with the fact that dimercuri-ammonium nitrite, which is derived from a single molecule of ammonium nitrite, contains half a molecule of water.

The filtrate was subjected to distillation, and the presence of ethyl alcohol in the distillate was proved by the iodoform test; it was no doubt derived from the decomposition of the ethylammonium nitrite.

It is of interest to note that whilst by the action of ammonia and alkylated ammonia on mercuric chloride the compounds $NHg''H_2Cl$ and $NHg''EtHCl$ respectively are formed, with mercuric nitrite there are always obtained products in which all the atoms of hydrogen of ammonium nitrite are displaced by mercury and alkyl radicles.*

We are engaged in studying the action of other alkylated ammonias on mercuric nitrite.

Chemical Laboratory,
Presidency College, Calcutta.

* In this communication we have used the term dimercuriammonium nitrite in preference to dimercurammonium nitrite, as the former appears to be in strict conformity with scientific nomenclature.

CCXXIV.—*Studies of Ammonium Solutions. Part I. An Ammonium Electrode.**

By Roland Edgar Slade.

It has been shown (Le Blanc, *Zeitsch. physikal. Chem.*, 1890, **5**, 467; Coehn, *Zeitsch. anorg. Chem.*, 1900, **25**, 430; Smith, *J. Amer. Chem. Soc.*, 1907, **29**, 844; see also McCoy and Moore, *ibid.*, 1911, **33**, 273) that ammonium, NH_4, behaves like a metal in that it is able to form an amalgam with mercury, and that NH_4 in this amalgam is able partly to displace sodium, potassium, and barium from aqueous solutions of their salts. From analogy it seemed probable that when ammonia and hydrogen were dissolved in platinum there would be some ammonium formed, and that there would be an equilibrium:

$$NH_3 + H \rightleftarrows NH_4$$

between ammonia, atomic hydrogen, and ammonium. It is known that hydrogen dissolved in platinum exists in the atomic state (Richardson, Nocol, and Parnell, *Phil. Mag.*, 1904, [vi], **8**, 1). If this equilibrium exists, a piece of platinised platinum saturated with hydrogen and ammonia would act as an ammonium electrode in a solution containing ammonium ions.

By Nernst's theory the potential, e, of this electrode would be:

$$e = -\frac{RT}{F}\ln\frac{k_1 C}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where: k is a constant.

C is the concentration of ammonium in the platinum.

c is the concentration of ammonium in the aqueous solution.

This potential will be that of the reaction:

$$2NH_3 + H_2 \longrightarrow 2NH_4^{\cdot} + 2\ominus,$$

and will vary with the partial pressures of NH_3 and H_2, and with the concentration of the ammonium ions in the aqueous solution. We will denote concentrations in the platinum by [ ]′, and in the aqueous solution by [ ], for instance, $[NH_3]'$ is the concentration of ammonia in the platinum, and $[NH_3]$ the concentration of ammonia in the aqueous solution.

If we have the equilibrium $NH_3 + H \rightleftarrows NH_4$ in the platinum:

$$[NH_4]' = k_2[H]'.[NH_3]' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* During the course of this investigation, Brönsted (*Zeitsch. physikal. Chem.*, 1911, **77**, 129) has published a paper on the free energy of formation of double salts in which he describes the use of a hydrogen electrode in ammonium chloride solutions under a definite partial pressure of ammonia.

The concentration of ammonia, NH_3, in the platinum will be proportional to the partial pressure of ammonia. Or:

$$[NH_3]' = kp_{NH_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

Therefore from (2) and (3):

$$[NH_4]' = k_2k_3[H]'.p_{NH_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

Now:

$$[H]' = k_4\sqrt{[H_2]'}$$

and

$$[H_2]' = k_5p_{H_2},$$

where p_{H_2} is the partial pressure of hydrogen over the platinum and solution.

Therefore:

$$[H]' = k_4k_5^{\frac{1}{2}}.p_{H_2}^{\frac{1}{2}},$$

and from (4):

$$[NH_4]' = k_2k_3k_4k_5^{\frac{1}{2}}p_{NH_3}p_{H_2}^{\frac{1}{2}}.$$

Therefore (1) becomes:

$$e = -\frac{RT}{F}\ln\frac{k_1k_2k_3k_4k_5^{\frac{1}{2}}p_{NH_3}p_{H_2},}{[NH_4^{\bullet}]}$$

or at 25° collecting the constants:

$$e = -0{\cdot}059\log\frac{kp_{NH_3}p_{H_2}^{\frac{1}{2}}}{[NH_4^{\bullet}]} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

Even if this electrode reaction $NH_4 \longrightarrow NH_4^{\bullet} + \ominus$ does not actually take place, the potential of the electrode will still be that of the reaction:

$$2NH_3 + H_2 \longrightarrow 2NH_4^{\bullet} + 2\ominus.$$

For if it is simply a hydrogen electrode, we have:

$$e = -0{\cdot}059\log\frac{k_6p_{H_2}^{\frac{1}{2}}}{[H^{\bullet}]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

But:

$$[H^{\bullet}] = \frac{K_w}{[OH^{\bullet}]}$$

and

$$[OH'].[NH_4'] = k_7[NH_4OH] = k_8[NH_3] = k_9p_{NH_3},$$

therefore:

$$[OH'] = \frac{k_9p_{NH_3}}{[NH_4^{\bullet}]}$$

and

$$[H^{\bullet}] = \frac{K_w.[NH_4^{\bullet}]}{k_9p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7).$$

From (6) and (7):

$$e = -0{\cdot}059\log\frac{k_6K_wp_{NH_3}p_{H_2}^{\frac{1}{2}}}{k_9[NH_4^{\bullet}]},$$

or collecting the constants:

$$e = -0{\cdot}059 \log \frac{k p_{NH_3} p^{\frac{1}{2}}_{H_2}}{[NH_4^{\cdot}]},$$

which is identical with (6). Therefore, whether the reaction is:

$$NH_4 \longrightarrow NH_4^{\cdot} + \ominus \quad \text{or} \quad H \longrightarrow H^{\cdot} + \ominus,$$

the potential measured is that of the chemical reaction:

$$2NH_3 + H_2 \longrightarrow 2NH_4^{\cdot}.$$

Experimental.

The solution for the cell was made up by weighing out a certain amount of ammonium chloride dissolving in a solution of ammonia of known strength, and making up to 100 c.c. with this solution. The partial pressure of ammonia over such a solution would be approximately that of the partial pressure of the original ammonia solution. By passing a stream of electrolytic gas through the pure ammonia solution and then through the ammonium chloride solution for some hours, the partial pressure over the latter solution was brought to be the same as that over the former. The arrangement was as follows: A gentle stream of electrolytic gas, prepared by the electrolysis of sodium hydroxide solution, was passed through (1) a wash-bottle of the type used by Gauss (*Zeitsch. anorg. Chem.*, 1900, **25**, 236) containing about 200 c.c. of a solution of ammonia of known concentration; (2) a similar wash-bottle containing the same solution; (3) a wash-bottle (ordinary type) containing ammonium chloride solution of the concentration under investigation; (4) the electrode vessel. After sixteen hours the ammonia solution in the first two wash-bottles was renewed, and a stream of hydrogen substituted for the electrolytic gas. The ammonium electrode was connected with a normal calomel electrode, and measurements of the *E.M.F.* made at intervals for several hours. The *E.M.F.* became constant in forty to fifty minutes, and remained quite steady to 0·3 m.v. The hydrogen was prepared by the action of pure dilute sulphuric acid on pure zinc; it was passed through alkaline permanganate solution, and then over red-hot copper gauze. The electrode vessels were of borosilicate glass.* The electrodes were platinised platinum. The electrode vessel and ammonia solutions were kept in a thermostat at 25°.

The potentials were measured by the compensation method, using a calibrated metre bridge and a galvanometer as null instrument. By means of a resistance in series with the bridge, the standard cell was balanced against about 90 cm. of the wire. The standard cadmium cell, which had been tested at the National Physical

* These vessels were made by Mr. Baumbach, of Manchester.

Laboratory, was taken as 1·0183 volts at 20°. The accuracy of measurement when the resistance of the cell was low was 0·1 m.v. Three normal calomel electrodes were made up as described in Ostwald-Luther's "Physico-Chemische Messungen" (1900). Three decinormal calomel electrodes were also made up. The normal calomel electrodes were tested from time to time against the decinormal electrodes, and were always found to give 0·0534 ± 0·0002 v.

The following cells were measured:

TABLE I.

	E observed.
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid N\text{-}NH_4Cl \mid H_2\ NH_3(2N)$	0·8604 volt
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid N\text{-}NH_4Cl \mid H_2\ NH_3(N)$	0·8401 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid N\text{-}NH_4Cl \mid H_2\ NH_3(0{\cdot}5N)$	0·8205 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid N\text{-}NH_4Cl \mid H_2\ NH_3(0{\cdot}05N)$	0·7622 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid N\text{-}NH_4Cl \mid H_2\ NH_3(0{\cdot}01N)$	0·7198 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid 0{\cdot}4N\text{-}NH_4Cl \mid H_2\ NH_3(2N)$	0·8848 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid 0{\cdot}4N\text{-}NH_4Cl \mid H_2\ NH_3(N)$	0·8631 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid 0{\cdot}4N\text{-}NH_4Cl \mid H_2\ NH_3(0{\cdot}5N)$	0·8426 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid 0{\cdot}4N\text{-}NH_4Cl \mid H_2\ NH_3(0{\cdot}05N)$	0·7847 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid 0{\cdot}4N\text{-}NH_4Cl \mid H_2\ NH_3(0{\cdot}01N)$	0·7436 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid 0{\cdot}08N\text{-}NH_4Cl \mid H_2\ NH_3(0{\cdot}05N)$	0·828 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid 0{\cdot}08N\text{-}NH_4Cl \mid H_2\ NH_3(0{\cdot}01N)$	0·788 ,,

$NH_3(2N)$ denotes that the partial pressure of ammonia over the solution was equal to that over a twice normal aqueous ammonia solution. The cells with $0{\cdot}08N\text{-}NH_4Cl$ had so great a resistance that the measurements were only correct to ±0·1 m.v.

The single potentials of the ammonium electrodes can be calculated from the above values by subtracting 0·283, which is the value of the single potential of the normal calomel electrode at 25°, taking the normal hydrogen electrode as zero. These values are given in table II under e.

From equation (5):

$$e = -0{\cdot}059 \log \frac{k p_{NH_3} p_{H_2}^{\frac{1}{2}}}{[NH_4^{\cdot}]}.$$

Therefore:

$$e = e_0 - 0{\cdot}059 \log \frac{p_{NH_3} p_{H_2}^{\frac{1}{2}}}{[NH_4^{\cdot}]}.$$

where e_0 is the normal potential of ammonium. It is the potential which a platinised platinum electrode would give in a solution normal in respect to ammonium ions, the partial pressures of ammonia and hydrogen over the solution being each one atmo-

sphere. In table II under e_0 are the values of this quantity calculated in each case by the equation:

$$e_0 = e + 0{\cdot}059 \log \frac{p_{NH_3} p_{H_2}^{\frac{1}{2}}}{[NH_4^{\cdot}]}.$$

Under $f(c)$ are given the values of

$$0{\cdot}059 \log \frac{p_{NH_3} p_{H_2}^{\frac{1}{2}}}{[NH_4^{\cdot}]}.$$

The *E.M.F.* of the liquid potentials has been neglected, as it is in all the cases considered not greater than one millivolt; the migration ratios of ammonium chloride and potassium chloride are both very nearly 0·5.

TABLE II.

		e.	$f(c)$.	$[NH_4^{\cdot}]$	p_{H_2}. in mm. of Hg.	p_{NH_3}	e_0.
NH_3 (2*N*)	H_2 | *N*-NH_4Cl ...	−0·577	0·089	0·8140	710	27·4	−0·488
NH_3 (*N*)	H_2 | *N*-NH_4Cl ...	−0·557	0·071	0·8135	723	13·52	−0·486
NH_3 (0·5*N*)	H_2 | *N*-NH_4Cl ...	−0·537	0·054	0·8127	730	6·71	−0·483
NH_3 (0·05*N*)	H_2 | *N*-NH_4Cl ...	−0·479	−0·005	0·8110	736	0·667	−0·484
NH_3 (0·01*N*)	H_2 | *N*-NH_4Cl ...	−0·437	−0·047	0·8104	736	0·1334	−0·484
NH_3 (2*N*)	H_2 | 0·4NH_4Cl ...	−0·602	0·111	0·3420	710	27·4	−0·491
NH_3 (*N*)	H_2 | 0·4NH_4Cl ...	−0·580	0·094	0·3415	723	13·52	−0·486
NH_3 (0·5*N*)	H_2 | 0·4NH_4Cl ...	−0·560	0·076	0·3408	730	6 71	−0·484
HH_3 (0·05*N*)	H_2 | 0·4NH_4Cl ...	−0·502	0·017	0·3390	736	0·667	−0·485
NH_3 (0·01*N*)	H_2 | 0·4NH_4Cl ...	−0·461	−0·024	0·3384	736	0·1334	−0·485
NH_3 (0·05*N*)	H_2 | 0·08NH_4Cl..	−0·545	0·056	0·0734	746	0·667	−0·489
NH_3 (0·01*N*)	H_2 | 0·08NH_4Cl..	−0·505	0·015	0·0728	736	0·1334	−0·490
						Mean.. ...	−0·486

Under $[NH_4^{\cdot}]$, p_{H_2}, and p_{NH_3} are given the values of these quantities used in calculating $f(c)$ and e_0. The values of $[NH_4^{\cdot}]$ were taken as the sum of the concentrations of the ions derived from the ammonium chloride and from the ammonia, as though each were independent of the other. It would perhaps be more correct in the strong ammonium chloride solutions to assume that the ammonia was quite inappreciably dissociated, since the high concentration of ammonium ions would throw back the dissociation. If we do this, however, it causes a difference of only 0·1 m.v. in the calculated values of $f(c)$. For the degree of dissociation of ammonium chloride at 0·4 and 0·08*N*, the results of Jones and West (*Amer. Chem. J.*, 1905, **34**, 557) were taken, and the value for *N*-ammonium chloride was obtained by extrapolating from their results. For the ionisation of ammonia, the values of Noyes, Kato, and Sosman (*J. Amer. Chem. Soc.*, 1910, **32**, 159) at 18° up to 0·5*N* were taken. The values for *N* and 2*N* were extrapolated from their values. The values of p_{NH_3} up to *N*-NH_3 were taken from Locke and Forsall

(*Amer. Chem. J.*, 1904, **31**, 268), and the value for $2N$ by extrapolating by the formula $p_{NH_3}=13{\cdot}34N+0{\cdot}18N^2$, where N is the normality of ammonia in the solution. In calculating the partial pressure of hydrogen, the vapour pressure of water and of the solutions at 25° was taken as 23 mm. The error introduced by this assumption is less than 0·1 m.v. in the case of N-ammonium chloride. These values were not corrected for changes of barometric pressure, or for the pressure in the electrode vessel being slightly greater than that of the atmosphere. Such differences make no appreciable difference in the value of $f(c)$.

Taking the mean of our values of e_0, we have for the potential of the ammonium electrode at 25°:

$$e = -0{\cdot}486 - 0{\cdot}059 \log \frac{p_{NH_3} p_{H_2}^{\frac{1}{2}}}{[NH_4^{\cdot}]}.$$

The agreement of the values of e_0 over wide ranges of concentration is better than for any other hydrogen electrode; for instance, compare the results collected by Wilsmore (*Zeitsch. physikal. Chem.*, 1900, **35**, 302). Moreover, the solutions here investigated were weakly alkaline, whilst Allmand (this vol., p. 842) found that the hydrogen electrode was particularly untrustworthy in dilute alkaline (sodium and potassium hydroxide) solutions. This steadiness of the electrode suggests the probability that the electrode reaction is chiefly $NH_4 \longrightarrow NH_4^{\cdot} + \ominus$, and not $H \longrightarrow H^{\cdot} + \ominus$.

Formation of Complexes.—In the above calculations the formula of the ammonium ion has been supposed to be NH_4, but in the presence of excess of free ammonia it is quite feasible to suppose that NH_3 might be added on, and we should get some complexes of the type $(NH_3)_xH^{\cdot}$. v. Braun (Abegg's "Handbuch," **3**, 74) states that it is not improbable that they exist at high concentrations. By the following method we can determine the average value of x in the solution. If there are no complexes, that is, if the only ions are $NH_4^{\cdot}$ or $NH_3H^{\cdot}$, we shall find $x=1$.

In the aqueous solution there must exist the equilibrium:

$$xNH_3 + H^{\cdot} \rightleftarrows (NH_3)_xH^{\cdot},$$

and therefore:

$$k[H^{\cdot}] = \frac{[(NH_3)_xH^{\cdot}]}{[NH_3]^x}.$$

In two solutions of different concentrations the ratio of the hydrogen ion concentrations:

$$\frac{[H^{\cdot}]_1}{[H^{\cdot}]_2} = \frac{[(NH_3)_xH^{\cdot}]_1}{[(NH_3)_xH^{\cdot}]_2} \frac{[NH_3]_2^x}{[NH_3]_1^x}.$$

Taking logarithms:

$$\log\frac{[H^\cdot]_1}{[H^\cdot]_2} = \log\frac{[(NH_3)_xH^\cdot]_1}{[(NH_3)_xH^\cdot]_2} - x\log\frac{[NH_3]_1}{[NH_3]_2} \quad . \quad . \quad (8).$$

If, however, the two solutions have the same concentration of ammonium chloride, we have:

$$[(NH_3)_xH^\cdot]_1 = [(NH_3)_xH^\cdot]_2,$$

and from (8):

$$\log\frac{[H^\cdot]_1}{[H^\cdot]_2} = -x\log\frac{p_1}{p_2},$$

where p is the partial pressure of ammonia.

Therefore:

$$x = \frac{\log\frac{[H^\cdot]_1}{[H^\cdot]_2}}{\log\frac{p_2}{p_1}}$$

If we measure of *E.M.F.* of a cell of the type:

$$NH_3(p_1)H_2 \,|\, NH_4Cl \,|\, H_2NH_3(p_2),$$

we can calculate the value of $\log\frac{[H^\cdot]_1}{[H^\cdot]_2}$, for the cell consists of two hydrogen electrodes each with hydrogen at the same pressure, but surrounded by solutions of different hydrogen ion concentration; thus:

$$\log\frac{[H^\cdot]_1}{[H^\cdot]_2} = +\frac{e}{0{\cdot}059}.$$

The values of p_1 and p_2 may be determined as above; x may then be calculated.

In table III are given the values of e observed, and the values of x calculated from them. The value of e was not directly measured; each half of the cell was measured against a normal calomel electrode. The observations are given in table I.

TABLE III.

Cell.					e.	x.
NH_3 (2*N*)	H_2 |	*N*-NH_4Cl |	H_2	NH_3 (*N*)	−0·020	1·18
NH_3 (2*N*)	H_2 |	0·4 *N*-NH_4Cl |	H_2	NH_3 (*N*)	−0·022	1·21
NH_3 (*N*)	H_2 |	*N*-NH_4Cl |	H_2	NH_3 (0·5*N*)	−0·020	1·09
NH_3 (*N*)	H_2 |	0·4 *N*-NH_4Cl |	H_2	NH_3 (0·5*N*)	−0·020	1·09
NH_3 (0·5*N*)	H_2 |	*N*-NH_4Cl |	H_2	NH_3 (0·05*N*)	−0·058	0·99
NH_3 (0·5*N*)	H_2 |	0·4 *N*-NH_4Cl |	H_2	NH_3 (0·05*N*)	−0·058	0·99
NH_3 (0·05*N*)	H_2 |	*N*-NH_4Cl |	H_2	NH_3 (0·01*N*)	−0·042	1·03
NH_3 (0·05*N*)	H_2 |	0·4 *N*-NH_4Cl |	H_2	NH_3 (0·01*N*)	−0·041	1·00
NH_3 (0·05*N*)	H_2 |	0·08*N*-NH_4Cl |	H_2	NH_3 (0·01*N*)	−0·040	0·97

The values of x are almost exactly unity in the more dilute solutions, although there seems to be a slight tendency to form complexes in the more concentrated solutions. It will be noticed that in the above calculation the pressure of hydrogen has been

assumed to be the same over both electrodes in any one cell. The errors introduced by this assumption are of the order of 1 per cent. in the first and second cells, and quite negligible in the other cells.

In solutions containing no ammonium chloride, that is, in solutions of ammonia in pure water, we have $[OH'] = [(NH_3)_xH^{\cdot}]$, since the concentration of $H^{\cdot}$ is negligible compared with the concentration of ammonium ions. Therefore equation (8) becomes:

$$\log\frac{[H^{\cdot}]_1}{[H^{\cdot}]_2} = \log\frac{[OH']_1}{[OH']_2} - x\log\frac{p_1}{p_2}.$$

But $[OH'] = \frac{K_w}{[H^{\cdot}]}$ where K_w is a constant.

Therefore:

$$2\log\frac{[OH']_2}{[OH']_1} = -x\log\frac{p_1}{p_2},$$

and

$$x = 2\frac{\log\frac{[OH']_1}{[OH']_2}}{\log\frac{p_1}{p_2}},$$

We can calculate some values of x in pure ammonia solutions by this formula from the results of Noyes, Kato, and Sosman on the ionisation of ammonia solutions, and a knowledge of the pressure of ammonia over the solutions. The data are only available up to $0{\cdot}5N$-ammonia. The values obtained are all approximately unity.

Summary.

The potential of the ammonium electrode at 25° has been determined, and has been shown to depend upon the partial pressures of hydrogen and ammonia, and on the concentration of ammonium ions in the following way:

$$e = -0{\cdot}486 - 0{\cdot}059\log\frac{p_{NH_3}p_{H_2}^{\frac{1}{2}}}{[NH_4^{\cdot}]}.$$

where $e = e_{\text{electrode}} - e_{\text{solution}}$, and the potential of the hydrogen electrode in a solution of normal hydrogen ion concentration is taken as zero.

It has been shown that complexes of the form $(NH_3)_xH^{\cdot}$, where x is greater than one, do not exist to any appreciable extent in dilute aqueous ammonia or ammoniacal ammonium chloride solutions, although there is some evidence of their existence at higher concentrations.

Part of the expenses of this research were borne by a grant from the Chemical Society.

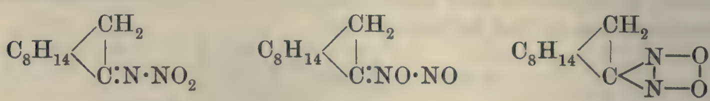
The author wishes to thank Professor F. G. Donnan for his kind interest in this work, and Mr. R. Kingan for some assistance in the experimental work.

THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,
UNIVERSITY OF LIVERPOOL.

CCXXV.—*Studies in the Camphane Series. Part XXX. Constitution of Pernitrosocamphor (Camphenylnitroamine).*

By MARTIN ONSLOW FORSTER, JOHN ROBERT TROTTER, and JACOB WEINTROUBE.

PERNITROSOCAMPHOR or camphenylnitroamine, discovered by Angeli and Rimini (*Ber.*, 1895, **28**, 1077), and independently by Tiemann (*loc. cit.*, 1079), is produced in association with camphorimine nitrite by the action of nitrous acid on camphoroxime, which also yields the pernitroso-derivative under the influence of dilute nitric acid or of nitrogen peroxide (Trans., 1897, **71**, 197). It has been the subject of numerous inquiries, notably by Hantzsch and Dollfus (*Ber.*, 1902, **35**, 260), Scholl (*Annalen*, 1905, **338**, 1; 1906, **345**, 363), Angelucci (*Annalen*, 1905, **341**, 172), Angeli and Castellana (*Atti R. Accad. Lincei*, 1905, [v], **14**, 669), who directed their efforts principally towards elucidating the problem of atomic arrangement in the N_2O_2-group. Without following the ramifications of this discussion, it may be stated that at present the rival formulæ are:



Hantzsch; Scholl. Angelucci. Angeli and Castellana.

The expression originally used by Tiemann, $C_8H_{14}<\begin{matrix}CH\\ \|\\ C\cdot NH\cdot NO_2\end{matrix}$, in conformity with which he called the substance camphenylnitroamine, no longer meets with favour, although its tautomeric form, $C_8H_{14}<\begin{matrix}CH\\ \|\\ C\cdot N\colon NO\cdot OH\end{matrix}$, is the one used by Hantzsch (*loc. cit.*) in representing the potassium derivative.

In spite of the labour which has been already expended on the problem, it cannot be said that the position is a satisfactory one, and it is difficult to see how a definite conclusion is to be drawn between the nitroimine (Hantzsch and Scholl) and pernitroso-formula (Angeli and Castellana). It is not claimed that the present communication offers a final settlement, but we believe that the fresh material brought forward serves to emphasise an aspect of the question which has hitherto escaped the attention it deserves.

Very soon after the discovery of the substance it was found that the potassium derivative may be readily oxidised to camphoric acid (Mahla and Tiemann, *Ber.*, 1896, **29**, 2811), a fact which confirmed Tiemann in his representation; we find that if potassium ferricyanide is used, camphorquinone is the principal product, which somewhat discounts the presence of an ethenoid linking. Both experiments, however, seem to indicate that in the potassium derivative there exists an association between the pernitroso-group and the second carbon atom (the α-position in camphor) closer than has been hitherto suspected. A more convincing indication of this is to be found in the behaviour of potassium pernitrosocamphor towards diazonium salts. We find that on mixing neutral or slightly alkaline cold aqueous solutions of these materials, there takes place a coupling process, in which the arylazo-group attaches itself to the second carbon atom, leaving the pernitroso-group intact, the products having the properties of camphorquinonearylhydrazones, in which the oxygen is replaced by the pernitroso-group; by the action of hydroxylamine and of semicarbazide on these pernitrosocamphorquinonearylhydrazones, oximes and semicarbazones of the respective camphorquinonearylhydrazones are formed, and in this way there has been obtained, for example, the oxime of camphorquinonephenylhydrazone, previously prepared by the action of hydroxylamine on camphorquinonephenylhydrazone itself (Trans., 1909, **95**, 955):

$$C_8H_{14}<\begin{matrix}CH_2\\ |\\ C{:}N_2O_2\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}C{:}N\cdot NH\cdot C_6H_5\\ |\\ C{:}N_2O_2\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}C{:}N\cdot NH\cdot C_6H_5\\ |\\ C{:}NOH\end{matrix}$$

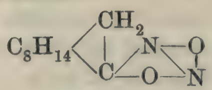
Furthermore, by the action of nitrosyl chloride on potassium pernitrosocamphor, there arises the pernitroso-derivative of *iso*nitrosocamphor, which likewise exchanges the pernitroso-nucleus for the oximino-group under the influence of hydroxylamine, leading to the β-dioxime of camphorquinone:

$$C_8H_{14}<\begin{matrix}CH_2\\ |\\ C{:}N_2O_2\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}C{:}NOH\\ |\\ C{:}N_2O_2\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}C{:}NOH\\ |\\ C{:}NOH\end{matrix}$$

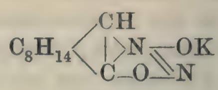
Thus it appears that the replacement of oxygen in camphor by the pernitroso-group confers on the α-position properties recalling

those of the CH_2-group in ethyl malonate, barbituric acid, nitroethane, and kindred substances, with, however, this difference, that pernitrosocamphor does not undergo condensation with benzaldehyde or with *p*-nitrosodimethylaniline.

Although it is not necessary to suppose that in pernitrosocamphor itself there is any direct association between the *α*-position and the pernitroso-group, it is difficult to believe that the potassium derivative could take part in such changes unless this connexion has been established, and we therefore suggest that the existing knowledge of these substances may be brought into harmony with the formulæ:



and



Pernitrosocamphor. Potassium derivative.

The above representation of pernitrosocamphor is in agreement with the direct production of the substance from camphoroxime and nitrosyl chloride (Angelucci), and is free from the objection which attaches to regarding the substance as a nitrite of camphoroxime. This latter view is discounted by the following circumstance. If pernitrosocamphor were the nitrite of camphoroxime, alcoholic alkali hydroxide should hydrolyse it to the original oxime, whereas we find that under conditions which leave camphoroxime unchanged, camphor itself is the only product. On the other hand, Angelucci's experiment may be used as an argument in support of the new formula, which might arise from the nitrite of camphoroxime by the mutual satisfaction of the partial valency existing in the two unsaturated linkings which that substance would present:

Camphoroxime nitrite. Pernitrosocamphor.

Moreover, the attachment simultaneously to nitrogen and oxygen, which characterises the carbon atom bearing the pernitroso-group, would in some measure explain the facility with which that group is removed by alkalis, amines, hydroxylamine, and semicarbazide, at the same time accounting for the production of camphoroxime, camphanazine, and the isomeric bornylamines by reducing agents, as observed by Angeli and Castellana.

Whilst it has to be admitted that the suggested formulæ for pernitrosocamphor and its potassium derivative are purely speculative, the same remark applies to those which have been put forward by other workers. They seem to us, however, to offer fewer steric

obstacles to the explanation of the facts. For instance, passage from the labile to the stable form of pernitrosocamphor would be comparatively smooth:

Labile. Stable.

the explanation given by Hantzsch and by Scholl involving a more profound intramolecular disturbance. Moreover, production of the pernitrosocamphorquinonearylhydrazones from the potassium derivative and diazonium salts would harmonise with the mechanism of coupling brought to light by Dimroth and Hartmann (*Ber.*, 1908, **41**, 4012), who showed that when benzenediazonium chloride couples with enolic tribenzoylmethane, a benzene-*O*-azo-compound is formed first, and changes into the isomeric benzene-*C*-azo-compound on fusion. The transference of the benzeneazo-nucleus from oxygen over nitrogen to carbon in enolic pernitrosocamphor is a process more readily conceivable than the alternative explanations, which involve a more circuitous route.

Experimental.

Pernitrosocamphorquinonephenylhydrazone,

$$C_8H_{14}<\begin{array}{l}C{:}N\cdot NH\cdot C_6H_5\\ |\\ C{:}N_2O_2\end{array}.$$

A solution of benzenediazonium chloride prepared from 4 grams of aniline was treated at zero with a 20 per cent. solution of sodium carbonate until neutral or faintly alkaline, and then poured into a cold solution of the potassium derivative of pernitrosocamphor (10 grams) in water. The product was a sticky, yellow mass, which was washed by decantation with ice-cold water, and afterwards rubbed with a very small quantity of alcohol, the resulting crystals being drained on porous earthenware; having been treated in this way three or four times, the product was dissolved in cold acetone, from which water precipitated golden-brown crystals. After recrystallisation from warm benzene the compound melted at 104°:

0·1729 gave 28·8 c.c. N_2 at 21° and 745 mm. N = 18·65.

$C_{16}H_{20}O_2N_4$ requires N = 18·66 per cent.

It is noteworthy that on combustion the substance liberates oxygen, which is apt to escape the copper spiral, and indicate a high percentage of nitrogen; the above result, for example, is reduced from over 21 per cent. by absorption with potassium pyrogallate. The substance dissolves readily in organic media, excepting petroleum; a solution containing 0·0997 gram, made up

to 20 c.c. with chloroform, gave α_D 1°52′ in a 1-dcm. tube, whence $[\alpha]_D$ 374·4°. Distinctive colour reactions are given with nitric and sulphuric acids, the latter producing a colour which is intense purple by reflected, deep blue by transmitted light; dilution with water changes this to bright yellow, becoming claret-colour with potassium hydroxide. A solution in concentrated nitric acid is claret-colour by reflected, green by transmitted light, green flocks separating on dilution with water.

Action of Hydroxylamine.—A solution of the pernitroso-derivative in dry pyridine containing excess of free hydroxylamine was allowed to remain during four weeks at 40°, when precipitation with water gave yellow needles, melting at 195°, identical with the oxime of camphorquinonephenylhydrazone already described (*loc. cit.*). The same compound was formed on heating an alcoholic solution of the pernitroso-derivative with aqueous hydroxylamine acetate during two to three hours.

Semicarbazone of Camphorquinonephenylhydrazone,

$$C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot C_6H_5 \\ | \\ C:N\cdot NH\cdot CO\cdot NH_2\end{matrix}.$$

The pernitroso-derivative was dissolved in alcohol, and heated with aqueous semicarbazide acetate under reflux during twenty hours; the filtered liquid gave a crystalline residue on evaporation, this being washed with water, and recrystallised from alcohol, which deposited lustrous, golden-yellow, six-sided plates, melting at 268°:

0·1176 gave 24·1 c.c. N_2 at 18° and 746 mm. N = 23·17.

$C_{17}H_{23}ON_5$ requires N = 22·36 per cent.

The semicarbazone dissolves freely in cold acetone, but less readily in hot alcohol; it is sparingly soluble in boiling benzene, and insoluble in hot petroleum. Concentrated nitric acid develops a green coloration.

Pernitrosocamphorquinone-p-*nitrophenylhydrazone*,

$$C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot C_6H_4\cdot NO_2 \\ | \\ C:N_2O_2\end{matrix}.$$

On attempting to couple the pernitroso-compound with diazotised *p*-nitroaniline, the product was very sticky, as before, but could not be crystallised. By adding the solution of potassium pernitrosocamphor (10 grams) to the neutralised solution of *p*-nitrobenzenediazonium chloride (prepared from 5·9 grams of *p*-nitroaniline), instead of vice versa, however, the derivative was precipitated in separate particles; after treatment with a small quantity of cold

methyl alcohol, the drained substance was recrystallised from benzene, being deposited in yellow prisms, melting at 96°:

0·1146 gave 18·4 c.c. N_2 at 19° and 747 mm. N = 18·15.

$C_{16}H_{19}O_4N_5$ requires N = 20·29 per cent.

The deficit in nitrogen was shown to be due to solvent of crystallisation, for the substance, after being heated or kept in a desiccator, melted at 178°:

0·9040 lost 0·0959 during five hours at 70°. Loss = 10·61.

0·1470 (residue) gave 26·4 c.c. N_2 at 17° and 764 mm. N = 20·86.

$C_{16}H_{19}O_4N_5 + \frac{1}{2}C_6H_6$ requires loss = 10·16; N = 18·22 per cent.

$C_{16}H_{19}O_4N_5$ requires N = 20·29 per cent.

The substance is readily soluble in acetone and in hot benzene, but is insoluble in petroleum.

Oxime of Camphorquinone-p-*nitrophenylhydrazone*,

$$C_8H_{14}<\begin{matrix}C{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2 \\ | \\ C{:}NOH\end{matrix}.$$

On heating an alcoholic solution of pernitrosocamphorquinone-*p*-nitrophenylhydrazone with aqueous hydroxylamine acetate during some hours, the liquid deposited on evaporation a residue which hardened when treated several times with water; recrystallisation from alcohol gave brown needles, melting at 186°:

0·2057 gave 32·3 c.c. N_2 at 18·5° and 755 mm. N = 18·02.

$C_{16}H_{20}O_3N_4$ requires N = 17·72 per cent.

The substance forms a cherry-red solution in concentrated sulphuric acid, whilst alcoholic ammonia develops a brilliant carmine. It dissolves readily in hot alcohol and in cold chloroform or ethyl acetate, but is more sparingly soluble in boiling benzene, and is insoluble in hot petroleum.

Semicarbazone of Camphorquinone-p-*nitrophenylhydrazone*,

$$C_8H_{14}<\begin{matrix}C{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2 \\ | \\ C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2\end{matrix}.$$

This substance was produced on replacing hydroxylamine in the foregoing reaction by semicarbazide; it crystallised from alcohol in golden-yellow plates, melting and decomposing at 250°:

0·1154 gave 23·6 c.c. N_2 at 20° and 755 mm. N = 23·24.

$C_{17}H_{22}O_3N_6$ requires N = 23·45 per cent.

The semicarbazone is freely soluble in cold acetone, but dissolves less readily in chloroform, and only sparingly in boiling benzene; it is insoluble in petroleum. Concentrated sulphuric acid develops an intense, cherry-red coloration, alcoholic ammonia giving a more brownish-red.

Pernitrosocamphorquinone-p-*bromophenylhydrazone*,

$$C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot C_6H_4Br \\ | \\ C:N_2O_2\end{matrix}.$$

This derivative was obtained in two modifications, which differ distinctly from one another in fusibility and specific rotatory power. The product separated in the form of a bright yellow, granular precipitate on adding aqueous potassium pernitrosocamphor to diazotised *p*-bromoaniline rendered alkaline with sodium carbonate; it altered on the filter to a hard, brown cake, which was treated with cold acetone. The undissolved portion was crystallised from benzene by adding petroleum, which precipitated golden-yellow, transparent prisms, melting at 143° with vigorous intumescence:

0·1563 gave 20·5 c.c. N_2 at 17° and 746 mm. N = 14·91.
0·2780 „ 0·1378 AgBr. Br = 21·09.
$C_{16}H_{19}O_2N_4Br$ requires N = 14·77; Br = 21·11 per cent.

A solution containing 0·2941 gram, made up to 25 c.c. with chloroform, gave α_D 7°5′ in a 2-dcm. tube, whence $[\alpha]_D$ 301·0°, this value remaining unaltered during ten days. The substance develops an intense, chocolate-brown coloration with concentrated sulphuric acid, changing to weak claret colour, with faint green dichroism, on adding nitric acid.

The acetone filtrate from the foregoing substance deposited a dark brown oil on evaporation, this becoming solid when stirred with dilute hydrochloric acid; recrystallisation from benzene to which petroleum was added gave clear-cut, yellow, transparent prisms, melting at 159°:

0·1823 gave 24·4 c.c. N_2 at 19° and 737 mm. N = 14·91.
0·3326 „ 0·1642 AgBr. Br = 21·01.
$C_{16}H_{19}O_2N_4Br$ requires N = 14·77; Br = 21·11 per cent.

A solution containing 0·2335 gram, made up to 25 c.c. with chloroform, gave α_D 5°50′ in a 2-dcm. tube when examined immediately; in the course of ten days this had fallen to 4°24′, when the liquid was almost too dark to transmit the necessary light. The initial and final readings correspond with $[\alpha]_D$ 312·3° and 235·5° respectively. In recrystallising the substance from a mixture of benzene and petroleum, it was noticed that nodules separated first, followed by silky, yellow needles; no other difference could be detected between these two forms, and on one occasion when a mixture of nodules and needles had separated, the former changed into the latter during one night in the mother liquor.

The dichroism of the bromo-derivative of higher melting point in sulphuric-nitric acid is distinct from that of the more fusible

one, the secondary colour being bright blue. The principal difference between the two substances, however, lies in the behaviour towards petroleum (b. p. 60—80°); this does not dissolve the derivative of higher melting point, whilst 1 gram of the isomeride requires less than 100 c.c. of the boiling solvent for dissolution, separating in lustrous, six-sided plates.

Oxime of Camphorquinone-p-*bromophenylhydrazone*,

$$C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot C_6H_4Br\\ |\\ C:NOH\end{matrix}.$$

This substance, prepared from the higher melting bromophenylhydrazone and hydroxylamine acetate in aqueous alcohol, crystallised from alcohol in rectangular, primrose prisms, melting at 180°:

0·1989 gave 21·8 c.c. N_2 at 19° and 738 mm. N = 12·25.

$C_{16}H_{20}ON_3Br$ requires N = 12·00 per cent.

A solution containing 0·1950 gram, made up to 20 c.c. with chloroform, gave α_D 4°13′ in the 2-dcm. tube, whence $[\alpha]_D$ 215·5°. An intense, red coloration is developed by concentrated sulphuric acid, and is bleached on adding nitric acid. The oxime is very sparingly soluble in boiling petroleum, but dissolves freely in cold acetone, chloroform, methyl alcohol, ethyl acetate, or boiling benzene.

Semicarbazone of Camphorquinone-p-*bromophenylhydrazone*,

$$C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot C_6H_4Br\\ |\\ C:N\cdot NH\cdot CO\cdot NH_2\end{matrix}.$$

This was also prepared from the less fusible bromophenylhydrazone, and crystallised from alcohol in brown, six-sided plates, melting at 265°:

0·1481 gave 22·7 c.c. N_2 at 18° and 760 mm. N = 17·70.

$C_{17}H_{22}ON_5Br$ requires N = 17·85 per cent.

The substance is insoluble in petroleum, and dissolves only sparingly in boiling benzene; it is moderately soluble in hot methyl alcohol.

Pernitrosocamphorquinoneoxime (*Pernitroso*iso*nitrosocamphor*),

$$C_8H_{14}<\begin{matrix}C:NOH\\ |\\ C:N_2O_2\end{matrix}.$$

Preliminary experiments showed that there is not any action between potassium pernitrosocamphor and amyl nitrite, even in presence of sodium ethoxide, but nitrosyl chloride, although regenerating a considerable proportion of pernitrosocamphor, leads also to the *iso*nitroso-compound.

Ten grams of the potassium derivative suspended in dry ether were subjected to the action of nitrosyl chloride gas until the liquid became yellow, when it was shaken with dilute sodium hydroxide, and left about 5 grams of pernitrosocamphor on evaporation; the alkaline solution was bright yellow, and gave a bulky, colourless precipitate with hydrochloric acid, amounting, in various experiments, to between 1 and 3 grams. Recrystallisation from dilute alcohol gave colourless needles, petroleum depositing indefinite, fern-like crystals, resembling those of *iso*nitrosocamphor, and melting at 147·5°:

0·1418 gave 23·5 c.c. N_2 at 17° and 750 mm. N = 18·96.

$C_{10}H_{15}O_3N_3$ requires N = 18·66 per cent.

A solution containing 0·1415 gram, made up to 25 c.c. with chloroform, gave α_D 1°10′ in the 2-dcm. tube, whence $[\alpha]_D$ 103·1°. The substance is freely soluble in organic media, excepting petroleum, 250 c.c. of which (b. p. 80—100°) were required by 1·5 gram; it dissolves immediately in sodium hydroxide, developing a yellow coloration, and on adding freshly prepared ferrous sulphate solution to the diluted liquid there is a greenish-blue precipitate, rapidly becoming dark brown, quite distinct from the purple substance produced by *iso*nitrosocamphor in similar circumstances. On allowing an alcoholic solution to remain at 40° with excess of hydroxylamine acetate in water, camphorquinone-β-dioxime began to crystallise within two hours.

The *benzoyl* derivative, $C_8H_{14}<\begin{matrix}C:NO\cdot CO\cdot C_6H_5\\ | \\ C:N_2O_2\end{matrix}$, prepared from the sodium derivative and benzoyl chloride, dissolved with unexpected difficulty in hot alcohol, from which it crystallises in lustrous, transparent, six-sided prisms, becoming yellow and decomposing at 174°:

0·1792 gave 20·3 c.c. N_2 at 18° and 748 mm. N = 12·87.

$C_{17}H_{19}O_4N_3$ requires N = 12·62 per cent.

A solution containing 0·1491 gram, made up to 25 c.c. with chloroform, gave α_D 1°31′ in a 3-dcm. tube, whence $[\alpha]_D$ 84·7°. The substance is readily soluble in chloroform, acetone, ethyl acetate, and warm benzene, sparingly so in boiling petroleum; on adding 20 per cent. sodium hydroxide to the boiling alcoholic solution there is developed the deep yellow coloration of the sodium derivative, showing that the rearrangement leading to the colourless benzoyl derivative of *iso*nitrosocamphor does not occur on benzoylating the pernitroso-compound.

Production of Camphor from Pernitrosocamphor.

Tiemann showed that hydriodic acid removes the pernitroso-group and regenerates camphor (*Ber.*, 1895, **28**, 1081), which was recognised also by Angeli and Castellana (*loc. cit.*) in the complex mixture of materials arising from the pernitroso-derivative by reduction; this includes the two isomeric bornylamines, camphoroxime, camphene, camphanazine, nitrous acid, and nitrogen. We find that whilst hydrogen sulphide is without action on pernitrosocamphor in alcoholic solution, addition of ammonia causes the liquid to turn red and evolve gas; evaporation of the alcohol leaves camphor, which is also regenerated easily and quantitatively from the pernitroso-derivative by the action of alcoholic sodium hydroxide. Three grams in 10 grams of alcohol were heated with 2 grams of sodium hydroxide in 8 grams of water during three hours under reflux, when distillation in steam gave the expected quantity of camphor; a control experiment in which camphoroxime was substituted for pernitrosocamphor showed that under the above conditions the oxime undergoes no change. Hence the production of camphor by hydrolysis cannot depend on intermediate formation of camphoroxime.

Aniline also may be used for the recovery of camphor from the pernitroso-derivative, doubtless owing to the production of phenyliminocamphane, $C_8H_{14}<\begin{matrix}CH_2\\|\\C:N\cdot C_6H_5\end{matrix}$, which might be expected to undergo hydrolysis with great facility. When alcoholic solutions are heated, gas is liberated, and after a short interval the liquid gives camphor with hydrochloric acid; another experiment, in which the two materials were left in contact during many months at laboratory temperature, gave crystals of camphor without addition of acid, suggesting that phenyliminocamphane must be a highly unstable substance.

Action of Hydrazine on Pernitrosocamphor.

Angeli and Castellana have shown (*loc. cit.*) that the action of hydrazine on pernitrosocamphor leads to camphanazine, and this we find to be the case if the materials are heated together; the following experiment, however, seems to indicate that this is a secondary product, arising from decomposition of the unstable camphorhydrazone, $C_8H_{14}<\begin{matrix}CH_2\\|\\C:N\cdot NH_2\end{matrix}$, recently isolated by Kijner (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 582). Five grams of potassium pernitrosocamphor were covered with hydrazine hydrate

(60 per cent.), and allowed to remain in a stoppered vessel. At first there was not any noticeable change, but gradually the pasty mass became inflated with gas, and in the course of several weeks the crystals disappeared, leaving a viscous oil floating on the liquid. After two months this was extracted with ether, washed with water until the latter was without action on Fehling's solution, and then recovered by evaporating the ether without heat; the viscous residue had an odour resembling that of bornylamine, and reduced ammoniacal silver oxide when heated, whilst oxidation with hot aqueous mercury acetamide led to camphor. The remainder was therefore shaken with benzoyl chloride in 10 per cent. sodium hydroxide, giving rise to camphor benzoylhydrazone (see below), indicating that camphorhydrazone had been produced by the action of hydrazine hydrate on pernitrosocamphor.

Camphor Benzoylhydrazone, $C_8H_{14}<\begin{matrix}CH_2 \\ | \\ C:N\cdot NH\cdot CO\cdot C_6H_5\end{matrix}$.

On allowing molecular proportions of pernitrosocamphor and benzoylhydrazine to remain a few days in aqueous alcohol, lustrous, silky needles separated, melting at 171° after recrystallisation from methyl alcohol:

0·2006 gave 18·2 c.c. N_2 at 22° and 768 mm. N = 10·39.

$C_{17}H_{22}ON_2$ requires N = 10·37 per cent.

A solution containing 0·3791 gram, made up to 25 c.c. with chloroform, gave α_D $-1°32'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-50·5°$. Whilst freely soluble in cold acetone and chloroform, benzene, alcohol, and ethyl acetate dissolve only moderate proportions, and it is sparingly soluble in boiling petroleum. Concentrated sulphuric acid hydrolyses the substance to camphor, hydrazine, and benzoic acid.

Royal College of Science, London.
South Kensington, S.W.

CCXXVI.—*The Constituents of the Seeds of* Casimiroa edulis.

By Frederick Belding Power and Thomas Callan.

The *Casimiroa edulis*, La Llave and Lejarza (Nat. Ord. *Rutaceae*), is a tree which is widely distributed throughout Mexico and Central America. It is known in Mexico by the vernacular names of "Chochitzapotl" and "Iztactzapotl," and in Guatemala as "Mato sano." Under the title of "Zapote blanco," the Pharmacopœia of Mexico recognises the fruit and the seed of the *Casimiroa*, indicating the former to be used as an anthelmintic and the latter as a vulnerary, for which purpose the kernels of the seed are roasted and powdered. The fruit, as the specific name of the plant denotes, is edible, and has an agreeable flavour, although it is stated to induce sleep, whereas it has been recorded that the kernels of the seed are deleterious or even fatal in their effects (Hernandez, *Rerum medicarum Novae Hispaniae thesaurus*, etc., *Romae*, 1651, *Lib.* III., p. 89).

The first chemical investigation of the seed of the *Casimiroa* was by José Sanchez, who, in a thesis published in Mexico in 1893, indicated the presence of a crystalline substance giving the general reactions of an alkaloid, together with two resins, an essential oil, fatty matter, gum, glucose, and starch. The alkaloidal substance was considered to be the probable source of the reputed physiological action of the seed. In 1898 a Commission was appointed in Mexico for the botanical and chemical study of the *Casimiroa*, and for the purpose of determining its therapeutic value. As a result of this inquiry, it was stated by Altamirano that the seed contains a glucoside, which, however, could be obtained only as a pale yellow, amorphous mass. This product, which he regarded as the active principle, possessed a taste which was at first sweet, but afterwards bitter and persistent. It was soluble in water and in alcohol, and its solution yielded precipitates with the usual alkaloid reagents. The results of a subsequent study by Bocquillon, in France, were incorporated in a thesis entitled, "Étude botanique et pharmacologique des Xanthoxyléas-Casimiroa," 1901, pp. 104, and more recently the subject has been investigated by Bickern (*Arch. Pharm.*, 1903, **241**, 166). A series of pharmacological investigations relating to the *Casimiroa* has furthermore been recorded by Robin and Coyon, by Chevalier, and by Vincent in *Bull. gén. de thérapeutique*, 1909, **158**, 16, 96, 193, 241, the last-mentioned author having also given a complete historical survey of the subject.

The chemical examination of *Casimiroa* seeds by Bickern (*loc. cit.*) was apparently conducted with a very small quantity of material, the amount not being directly stated; but from the results obtained he was led to conclude that they contain a "gluco-alkaloid," melting at 106°, to which he assigned the name "casimirin," and the formula $C_{30}H_{32}O_5N_2$. This formula, however, was based on but one analysis, and its theoretical percentage figures were incorrectly recorded. Nevertheless, the substance was stated to undergo hydrolysis by heating with 30 per cent. hydrochloric acid, with the formation of an alkaloid, $C_{54}H_{54}O_5N_4$, and dextrose, in accordance with the equation:

$$2C_{30}H_{32}O_5N_2 + H_2O = C_{54}H_{54}O_5N_4 + C_6H_{12}O_6.$$

In this case also a considerable discrepancy in the figures appears to exist, inasmuch as an analysis of the residual alkaloid indicated it to contain 73·2 per cent. of carbon, whereas the formula $C_{54}H_{54}O_5N_4$ requires $C = 77·3$ per cent. It would, moreover, be impossible for a substance of the composition $C_{30}H_{32}O_5N_2$ to yield dextrose on hydrolysis, inasmuch as it contains but five oxygen atoms.

Another compound described by Bickern (*loc. cit.*) was obtained by mixing the powdered seed with lime, and extracting with ether, when, on evaporating the solvent, a colourless substance was precipitated. The latter, when crystallised from chloroform, separated in colourless needles, melting at 207°, and to it the name "casimirol" and the formula $C_{27}H_{48}O_2$ were assigned. As this substance yielded colour reactions similar to those of the phytosterols, it was assumed to be related to that class of compounds.

It was furthermore noted by Bickern that the above-mentioned substances, as well as various ethereal and alcoholic extracts of the seed, were tested on animals by Professor Cloëtta, of Zurich, but were found to be devoid of any hypnotic action. On the other hand, Chevalier (*loc. cit.*, p. 96) was led to conclude from the results of his experiments on animals that the therapeutic value of *Casimiroa* seed is due to the essential oil and resin they contain (compare also *Lancet*, August 21st, 1909, p. 561).

From the preceding brief review of the literature it will be observed that the statements respecting the constituents and physiological action of *Casimiroa* seeds are very divergent, and, to a large extent, inconclusive. In view of the interest pertaining to the subject it was deemed desirable to submit these seed to a more complete examination, and the results are embodied in the present communication.

EXPERIMENTAL.

Inasmuch as the entire fruit of *Casimiroa edulis* could not conveniently be transported to this country, and the seed are considered to be the most active portion, a quantity of the latter was specially collected in Mexico for the purpose of the present investigation. The seed, which in size and shape somewhat resemble an almond, are provided with a grey, fibrous shell, enclosing a kernel, which is covered with a thin, brown membrane. The shells were found to represent about one-fifth the weight of the entire fresh seed, and they were separately examined.

I.—*Examination of the Kernels.*

Separation of an Enzyme.

A quantity (810 grams) of the kernels, representing 1 kilogram of the entire seed, was crushed, and macerated with water at the ordinary temperature for two days, the liquid being then expressed and filtered. To the filtered liquid, in which the presence of starch was indicated, about twice its volume of alcohol was added, when an abundant flocculent precipitate was produced. After about twenty-four hours the precipitate was collected, washed with a little alcohol, and dried, first on a porous plate, and finally in a vacuum over sulphuric acid. It could then be reduced to a light brown powder, and amounted to 9 grams, or 0·9 per cent. of the weight of entire seed employed.

The above-described product, when dissolved in water, yielded a solution which frothed strongly on agitation, and gave an abundant, white, curdy precipitate, both with hydrochloric acid and on boiling. It gave the biuret reaction, and also slowly hydrolysed amygdalin, thus proving the presence of an enzyme.

Preliminary Test for an Alkaloid.—A small portion (about 6 grams) of the dried kernels of the seed was treated with Prollius' fluid, and the resulting liquid tested in the usual manner for an alkaloid. The results obtained indicated the presence of a considerable proportion of such a substance.

For the purpose of a complete examination of the seed, the shells were first separated from the kernels, and a quantity of the latter, which, after being ground, amounted to 37·05 kilograms, was extracted by continuous percolation with hot alcohol until exhausted. In view of the asserted presence of a glucoside, or of a "glucoalkaloid," in the seed, and in order to preclude the hydro-

lysis of such a substance, all the preliminary operations were conducted as quickly as possible. After the removal of the greater portion of the alcohol, the amount of thin extract obtained was 11·45 kilograms.

Distillation of the Extract with Steam. Separation of an Essential Oil.

The entire amount of extract was subjected to distillation in a current of steam, and the distillate, which contained some oily drops in suspension, extracted with ether. After the removal of the solvent, a quantity (8 grams) of an oily liquid was obtained, which, when distilled under diminished pressure, passed over between 80° and 160°/25 mm., but for the most part below 130°/25 mm. This essential oil, when freshly distilled, had a pale yellow colour, but gradually darkened on keeping, even in absence of air. It possessed an agreeable, aromatic odour, and the following constants: $d = 0{\cdot}9574$ at 20°; $\alpha_D - 2°25'$ in a 25 mm. tube. It gave no coloration with ferric chloride, and did not respond to the test for furfuraldehyde.

Non-volatile Constituents of the Extract.

After the above-described operation, there remained in the distillation vessel a dark-coloured aqueous liquid (A), together with a quantity of a soft, oily resin (B). These products were separated, and the resin thoroughly washed with hot water, the washings being added to the main portion of the aqueous liquid.

Examination of the Aqueous Liquid (A).

The aqueous liquid was repeatedly extracted with large quantities of ether, and the ethereal liquid, after concentrating to a convenient bulk, was shaken successively with aqueous ammonium carbonate, sodium carbonate, and sodium hydroxide.

Isolation of a New Alkaloid, Casimiroine, $C_{24}H_{20}O_8N_2$.

On shaking the ethereal extract of the aqueous liquid with a concentrated solution of ammonium carbonate, a crystalline substance slowly separated, and remained suspended in the alkaline liquid. This substance was collected, and amounted to 2·8 grams. It crystallised very readily from alcohol or ethyl acetate, separating in rosettes of colourless needles, and melted at 196—197°. Although very sparingly soluble in water, its aqueous solution, when acidified, gave copious precipitates with the usual alkaloidal reagents, such

as solutions of iodine in potassium iodide, potassium-mercuric iodide, and picric acid:

0·1170 gave 0·2670 CO_2 and 0·0514 H_2O. C=62·2; H=4·9.
0·1322 „ 7·2 c.c. N_2 at 16° and 768 mm. N=6·4.
$C_{24}H_{20}O_8N_2$ requires C=62·1; H=4·3; N=6·0 per cent.

These results, together with a subsequent analysis of its aurichloride, indicate the above-described alkaloid to possess the formula $C_{24}H_{20}O_8N_2$, and, being a new compound, it is proposed to designate it *casimiroine*.

Casimiroine contains two methoxyl groups, as the following determination by Perkins's modification of the Zeisel method has shown:

0·2790 gave 0·2886 AgI. MeO=13·6.
$C_{22}H_{14}O_6N_2(OMe)_2$ requires MeO=13·4 per cent.

Casimiroine is a very weak base, since it is precipitated from its solution in concentrated hydrochloric acid by dilution with water. The only crystalline salts that could be obtained were the *picrate* and the *aurichloride*. The picrate, which was very sparingly soluble, crystallised in small, yellow needles, melting at 165°.

Casimiroine Aurichloride, $C_{24}H_{20}O_8N_2,HAuCl_4$.—This salt was prepared by adding a solution of gold chloride to a dilute solution of casimiroine in aqueous alcohol containing a little hydrochloric acid. The yellow precipitate thus produced was crystallised from alcohol, when the salt was obtained in handsome, orange-yellow needles, melting at 195—196°:

0·1508 gave 0·1998 CO_2 and 0·0460 H_2O. C=36·1; H=3·4.
0·1207 „ , on ignition, 0·0296 Au. Au=24·5.
$C_{24}H_{20}O_8N_2,HAuCl_4$ requires C=35·8; H=2·6; Au=24·5 per cent.

A solution of the alkaloid in chloroform was found to be devoid of optical activity.

When a little casimiroine, on a porcelain tile, is moistened with a drop of concentrated nitric acid, a yellow colour is first produced, which rapidly deepens to orange-red. With concentrated sulphuric acid the alkaloid, when similarly treated, develops a pale green colour, which, on the addition of a trace of nitric acid, immediately changes to a brilliant orange hue.

Hydrolysis of Casimiroine.

Formation of a New Base, Casimiroitine, $C_{23}H_{22}O_7N_2$.

On boiling casimiroine for several hours with an alcoholic solution of potassium hydroxide, and then adding a small quantity of water, long, glistening, hair-like needles separate from the liquid

on cooling. By the careful fractional crystallisation of this product from ethyl acetate it was observed not to be homogeneous, but to consist mainly of a substance which separated in stout prisms, melting at 171°, together with a small quantity of a substance which crystallised in fan-like tufts of slender needles, melting at 159°. Only the first-mentioned substance (m. p. 171°) was obtained in an amount sufficient for analysis. On recrystallising this from dilute alcohol, it was obtained, like the original product, in long, glistening, hair-like needles, which formed a felty mass, greatly resembling glass-wool:

0·2680, dried at 110° to a constant weight, lost 0·0188 H_2O. $H_2O = 7·0$.

0·1106 * gave 0·2561 CO_2 and 0·0540 H_2O. C = 63·1; H = 5·4.

0·1560 * ,, 8·6 c.c. N_2 at 12·5° and 774 mm. N = 6·6.

$C_{23}H_{22}O_7N_2$ requires C = 63·0; H = 5·0; N = 6·4 per cent.

$C_{23}H_{22}O_7N_2,2H_2O$ requires $H_2O = 7·6$ per cent.

The above-described hydrolytic product is thus shown to possess the formula $C_{23}H_{22}O_7N_2$, and, being a new compound, it may be designated *casimiroitine*. It appears to have been formed from casimiroine by the addition of a molecule of water and the elimination of a molecule of carbon dioxide, according to the following equation:

$$C_{24}H_{20}O_8N_2 + H_2O = C_{23}H_{22}O_7N_2 + CO_2.$$

When casimiroine is boiled for a few minutes with concentrated hydrochloric acid, it yields an acid which is very sparingly soluble in alcohol and water, and melts above 300°. The amount of material available did not permit of the further study of this reaction.

Isolation of Benzoic Acid.

The ammonium carbonate solution, from which the suspended alkaloid, casimiroine, had been removed by filtration, as already described, was acidified, when a quantity of dark, resinous material was precipitated. As nothing crystalline could be directly isolated from this product, it was dissolved in methyl alcohol, and dry hydrogen chloride passed into the hot solution. The esterified mixture was then poured into water and extracted with ether, the ethereal liquid being subsequently shaken with a dilute solution of sodium hydroxide. The non-phenolic portion of the product possessed the odour of methyl benzoate, and on hydrolysis yielded a small amount of an acid (m. p. 120°), which was identified as benzoic acid. The phenolic portion contained a substance which

* Anhydrous substance.

gave an intense violet coloration with ferric chloride, and was evidently salicylic acid, but the amount of the latter was too small to permit of its isolation.

The original ethereal extract of the aqueous liquid, which had been shaken with a solution of ammonium carbonate, as previously described, was subsequently extracted successively with aqueous sodium carbonate and sodium hydroxide. These alkalis, however, removed only dark-coloured, resinous material, and on finally evaporating the ethereal liquid it left but a slight, oily residue.

Isolation of a New Alkaloid, Casimiroedine, $C_{17}H_{24}O_5N_2$.

The original aqueous liquid, which had been completely extracted with ether, was next shaken repeatedly with hot amyl alcohol. A portion of the amyl-alcoholic extract was concentrated under diminished pressure to a small bulk, when, on cooling, a quantity of dark-coloured, solid material separated. On treating this with a small amount of cold alcohol, most of the colouring matter was removed, leaving a slightly coloured, apparently crystalline substance. After the separation of the latter, no other crystalline substance could be isolated from the dark-coloured material, even after heating it with 5 per cent. sulphuric acid. As the above-mentioned substance was readily soluble in dilute acids, its isolation was found to be most easily effected by shaking the amyl-alcoholic extract with aqueous 2 per cent. sulphuric acid until the acid liquid ceased to give a precipitate with an aqueous solution of iodine in potassium iodide, and the larger remaining portion of the extract was therefore treated in this manner. The sulphuric acid was subsequently removed from the aqueous liquid by means of barium hydroxide, and the excess of the latter by carbon dioxide, after which the liquid was filtered and concentrated. During the process of evaporation the substance separated in the form of crusts, and the total amount so obtained was 16 grams. The substance, which was found to contain nitrogen, was recrystallised from alcohol, when it separated in wart-like aggregates of very small needles, melting at 222—223°:

0·1613 gave 0·3587 CO_2 and 0·0980 H_2O. C = 60·6; H = 6·8.
0·1466 " 10·8 c.c. N_2 at 11° and 743 mm. N = 8·6.
$C_{17}H_{24}O_5N_2$ requires C = 60·7; H = 7·1; N = 8·3 per cent.

The above-described substance, which has thus been shown to be an alkaloid, evidently possesses the formula $C_{17}H_{24}O_5N_2$. As it is a new compound, it is proposed to designate it *casimiroedine*.

Casimiroedine is a fairly strong base, since it dissolves readily

in dilute acids, and on rendering the solution alkaline the alkaloid only slowly separates in the form of rosettes of needles. It is very sparingly soluble in chloroform, ether, benzene, ethyl acetate, or cold alcohol, but is readily soluble in hot alcohol, and amyl alcohol dissolves it freely.

A slightly acidified solution of casimiroedine, even when exceedingly dilute, gives a reddish-brown precipitate with a solution of iodine in potassium iodide, but potassium-mercuric iodide and picric acid only yield precipitates with a somewhat concentrated solution.

The alkaloid in acid solution was found to be optically active, and a determination of its rotatory power gave the following result:

0·4198, made up to 20 c.c. with 1 per cent. hydrochloric acid, gave α_D $-1°32'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-36·5°$.

Casimiroedine was found to contain no methoxyl group, and in its chemical behaviour is a very indifferent substance. No crystalline derivative could be prepared from it with the exception of the *aurichloride.*

Casimiroedine Aurichloride, $C_{17}H_{24}O_5N_2,HAuCl_4,2H_2O$.—On the addition of a concentrated solution of gold chloride to a fairly strong solution of casimiroedine in hydrochloric acid the aurichloride is precipitated as an oil, which crystallises on stirring. This salt is dissociated in contact with water, but could be crystallised from 20 per cent. aqueous hydrochloric acid, when it separated in bright yellow, microscopic needles, which melt indefinitely at about 90° in their water of crystallisation. After drying at 70°, however, the salt melts and completely decomposes at 145—148°:

0·0984, dried at 100° to a constant weight, lost 0·0054 H_2O. $H_2O = 5·5$.

0·0930 (dried salt) gave, on ignition, 0·0272 Au. Au = 29·2.

$C_{17}H_{24}O_5N_2,HAuCl_4,2H_2O$ requires $H_2O = 5·1$ per cent.

$C_{17}H_{24}O_5N_2,HAuCl_4$ requires Au = 29·2 per cent.

The original aqueous liquid, which had been completely extracted with both ether and amyl alcohol, as already described, was subsequently treated with a slight excess of solution of basic lead acetate. A voluminous, light brown precipitate was thus produced, which was collected, thoroughly washed, and decomposed with hydrogen sulphide, but it yielded nothing definite. The filtrate from the basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the excess of lead, and the filtered liquid concentrated under diminished pressure. It then formed a viscid syrup, which contained a considerable quantity of sugar,

since it readily yielded *d*-phenylglucosazone, melting at 205—207°. A portion of the syrup was heated for two hours with dilute sulphuric acid in a reflux apparatus, and then distilled in a current of steam. The distillate contained traces of formic and acetic acids, and on extracting the liquid remaining in the distillation flask with ether, only a further small amount of these acids was obtained. The aqueous liquid was finally treated with barium hydroxide for the removal of the sulphuric acid, filtered, and concentrated, but no crystalline product separated, even after keeping for a considerable time. There was therefore no evidence that the original aqueous liquid contained any substance of a glucosidic nature.

Examination of the Resin (B).

The resinous material, representing that portion of the alcoholic extract of the kernels of the seed which was insoluble in water, formed a soft, oily mass, and amounted to about 375 grams. It was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with light petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

This extract, after the complete removal of the solvent, was a thin, dark-coloured, oily product, amounting to 256 grams. It was digested with 1 litre of ether, when 3·2 grams of a white, apparently crystalline substance remained undissolved, and were collected. This was resolved by fractional crystallisation from alcohol into a substance which was obtained in the form of needles, melting at 196—197°, and amounting to 1·5 grams, and a substance which melted at 232—233°. The first-mentioned substance consisted of the previously described alkaloid, casimiroine, which had been isolated from the aqueous liquid, whilst the second substance was subsequently obtained in much larger amount from the ethereal extract of the resin, and will be further considered in connexion with the latter.

After the separation of the above-mentioned crystalline substances, the clear ethereal solution of the petroleum extract was shaken with aqueous ammonium carbonate, which, however, removed only traces of resinous material. On subsequently attempting to extract the ethereal liquid with sodium carbonate and sodium hydroxide, intractable emulsions were formed. The ether was therefore removed, and the residue hydrolysed by heating with a

solution of 90 grams of potassium hydroxide in one litre of alcohol. After the removal of the alcohol, water was added, and the alkaline liquid repeatedly extracted with ether.

Isolation of Sitosterol, $C_{27}H_{46}O,H_2O$.

The ethereal extract of the alkaline liquid was dried, and the solvent evaporated. A pale yellow, crystalline product was thus obtained, which was dissolved in hot alcohol, when, on cooling, a quantity (8·8 grams) of a substance separated in colourless plates. On recrystallising the substance from a mixture of ethyl acetate and dilute alcohol, it was obtained in needles, melting at 134—135°:

0·2263, on heating at 100°, lost 0·0114 H_2O. $H_2O = 5·0$.

0·1048 * gave 0·3218 CO_2 and 0·1153 H_2O. C = 83·7; H = 12·2.

$C_{27}H_{46}O,H_2O$ requires $H_2O = 4·5$ per cent.

$C_{27}H_{46}O$ requires C = 83·9; H = 11·9 per cent.

The substance was thus identified as a phytosterol, and it gave the colour reactions of that class of compounds.

A determination of its optical rotatory power gave the following result:

0·3118,* made up to 20 c.c. with chloroform, gave α_D −1°0′ in a 2-dcm. tube, whence $[\alpha]_D$ −32·1°.

The phytosterol gave an acetyl derivative, which separated from acetic anhydride in small needles, melting at 126—127°. Its identity with sitosterol was therefore established.

The original alcoholic mother liquor remaining from the crystallisation of the sitosterol was evaporated, when a quantity (10 grams) of viscid, oily material was obtained. This was found to consist chiefly of oxygenated substances, but nothing definite could be isolated from it.

Isolation of Ipuranol, $C_{23}H_{38}O_2(OH)_2$.

The alkaline liquid, from which the sitosterol had been removed by extraction with ether, was acidified, and the liberated fatty acids taken up with ether. The ethereal liquid contained a quantity of a dark-coloured, crystalline substance in suspension. This was collected, heated with alcohol for the removal of colouring matter, and then recrystallised from dilute pyridine, from which it separated in microscopic needles, melting at 280—285°. The amount of substance so obtained was 2·9 grams. (Found, C = 72·6; H = 10·4. Calc., C = 72·6; H = 10·5 per cent.)

* Anhydrous substance.

The above results, together with the colour reactions yielded by this substance, established its identity as ipuranol.

When heated with acetic anhydride it gave diacetylipuranol, which separated from alcohol in shining leaflets, melting at 166°. (Found, C = 69·7; H = 9·5. Calc., C = 69·8; H = 9·5 per cent.)

On heating the ipuranol, in pyridine solution, with benzoyl chloride, a *dibenzoyl* derivative was obtained, which, after crystallisation from a mixture of ethyl acetate and alcohol, separated in needles melting at 197°.

A determination of the optical rotatory power of the ipuranol gave the following result:

0·1708, made up to 20 c.c. with pyridine, gave α_D −0°41′ in a 2-dcm. tube, whence $[\alpha]_D$ −40·0°.

Identification of the Fatty Acids.

The ethereal liquid from which the ipuranol had been removed, as above described, was evaporated to a low bulk, and a large quantity of light petroleum added. This precipitated some resinous material, which was separated, after which the liquid was again evaporated. A quantity (105 grams) of fatty acids was thus obtained, which, when distilled under diminished pressure, passed over between 200° and 230°/12 mm.

In order to effect a separation of the solid and liquid acids, a portion (25 grams) of the mixture was converted into the lead salts, and the latter digested with ether, when the greater part dissolved. Both the soluble and insoluble portions were decomposed by hydrochloric acid, and the liberated fatty acids separately examined.

The Liquid Acids.—These acids, when distilled under diminished pressure, passed over between 235° and 250°/15 mm. as a yellow oil. An analysis and determination of the constants gave the following results:

0·1026 gave 0·2906 CO_2 and 0·1099 H_2O. C = 77·2; H = 11·9.

0·2646 absorbed 0·4120 iodine. Iodine value = 155·7.

0·3094 neutralised 0·0621 KOH. Neutralisation value = 200·7.

$C_{18}H_{34}O_2$ requires C = 76·6; H = 12·1 per cent. I.V. = 90·1; N.V. = 198·9.

$C_{18}H_{32}O_2$ requires C = 77·1; H = 11·4 per cent. I.V. = 181·4; N.V. = 200·4.

$C_{18}H_{30}O_2$ requires C = 77·7; H = 10·8 per cent. I.V. = 274·1; N.V. = 201·8.

These results would indicate that the liquid acids consist of a mixture of oleic, linolic, and linolenic acids.

The Solid Acids.—These acids, when crystallised from glacial acetic acid, separated in glistening leaflets, melting at 60—62°:

0·1030 gave 0·2875 CO_2 and 0·1194 H_2O. C=76·1; H=12·9.
0·2292 neutralised 0·0461 KOH. Neutralisation value=201·1.
$C_{16}H_{32}O_2$ requires C=75·0; H=12·5 per cent. N.V.=219·1.
$C_{18}H_{36}O_2$ „ C=76·1; H=12·7 „ „ N.V.=197·5.

The solid acids would thus appear to consist of a mixture of palmitic and stearic acids, the latter predominating.

Ethereal Extract of the Resin.

This extract, after the removal of the solvent, formed a brittle mass, which could readily be reduced to a light brown powder, and amounted to 75 grams. It was heated with 2 litres of alcohol, when the greater portion dissolved. The small insoluble portion (2·3 grams) was collected, and identified as ipuranol.

Isolation of a New Lactone, Casimirolid, $C_{24}H_{28}O_6$.

The above-mentioned hot alcoholic liquid deposited on cooling a quantity (22·1 grams) of well-developed crystals, which, when recrystallised from alcohol with the addition of a little animal charcoal, separated in colourless prisms, melting at 229—230°:

0·0960 gave 0·2448 CO_2 and 0·0594 H_2O. C=69·5; H=6·9.
0·1326, in 21·16 benzene, gave $\Delta t - 0·072°$. M.W.=426.
$C_{24}H_{28}O_6$ requires C=69·9; H=6·8 per cent. M.W.=412.

From these results it is evident that the above-described substance possesses the formula $C_{24}H_{28}O_6$, and that it is a new compound. Having ascertained that it is a lactone, as shown below, it is proposed to designate it *casimirolid.*

Casimirolid is readily soluble in ether, chloroform, and ethyl acetate. It is optically active, and a determination of its specific rotatory power gave the following result:

0·3856, made up to 25 c.c. with chloroform, gave α_D $-1°31'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-49·2°$.

Hydrolysis of the Lactone.

Formation of a New Hydroxy-acid, Casimiroic Acid, $C_{23}H_{28}O_4(OH)\cdot CO_2H$.

When casimirolid is shaken with a cold solution of potassium hydroxide in aqueous alcohol, it readily takes up a molecule of water, and is converted into an acid, which is precipitated on acidifying the alkaline liquid. This acid crystallises very readily from alcohol in rosettes of glistening needles, melting at 207°:

0·1074 gave 0·2638 CO_2 and 0·0698 H_2O. C = 67·0; H = 7·2.

0·2792 neutralised 0·0359 KOH. M.W. (monobasic acid) = 436.

$C_{24}H_{30}O_7$ requires C = 67·0; H = 7·0 per cent. M.W. = 430.

The above-described acid is thus shown to possess the formula $C_{24}H_{30}O_7$. Like the corresponding lactone, it is a new compound, and it is proposed to designate it *casimiroic acid*.

A determination of the optical rotatory power of the acid gave the following result:

0·1670, made up to 20 c.c. with absolute alcohol, gave α_D $-1°27'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-86·8°$.

Casimiroic acid, unlike the lactone, is very sparingly soluble in ether, chloroform, and ethyl acetate. Its sodium salt is very readily soluble in water and in alcohol. On the addition of a solution of copper sulphate to a neutral solution of the sodium salt, a pale blue, amorphous precipitate of copper casimiroate was produced, the analysis of which, however, indicated it to consist of a basic salt.

Silver Casimiroate, $C_{23}H_{29}O_5 \cdot CO_2Ag$.—This salt was obtained as a white, amorphous precipitate on the addition of a solution of silver nitrate to a solution of the sodium salt. It is sparingly soluble in water, and gradually darkens on exposure to light:

0·1435 of salt gave, on ignition, 0·0296 Ag. Ag = 20·6.

$C_{24}H_{29}O_7Ag$ requires Ag = 20·1 per cent.

Methyl Casimiroate, $C_{23}H_{29}O_5 \cdot CO_2 \cdot CH_3$.—This ester was prepared by passing dry hydrogen chloride into a solution of the acid in methyl alcohol at the boiling temperature. It was very soluble in alcohol, and could only be obtained with difficulty in a crystalline state from dilute alcohol, when it melted at 108—110°:

0·1086 gave 0·2666 CO_2 and 0·0739 H_2O. C = 66·9; H = 7·6.

$C_{25}H_{32}O_7$ requires C = 67·5; H = 7·2 per cent.

Acetylcasimiroic Acid, $C_{23}H_{28}O_4(O \cdot CO \cdot CH_3) \cdot CO_2H$.—This was obtained by heating casimiroic acid with acetic anhydride, pouring the product into water, and digesting the resulting precipitate with dilute aqueous sodium carbonate, when, on acidifying the alkaline liquid, the *acetyl* derivative was precipitated. It was exceedingly soluble in the usual organic solvents, but could be obtained from dilute alcohol in colourless, microscopic needles. The acetyl derivative has no sharp melting point, but gradually decomposes at temperatures above 142°:

0·1149 gave 0·2774 CO_2 and 0·0738 H_2O. C = 65·8; H = 7·1.

$C_{26}H_{32}O_8$ requires C = 65·8; H = 6·8 per cent.

Isolation of a Yellow Phenolic Substance, $C_{16}H_{12}O_6$.

After the separation of the lactone, casimirolid, from the alcoholic solution of the ethereal extract of the resin, as previously described, the solvent was removed, and the residue, which still contained a small amount of lactone, dissolved in ether. The ethereal liquid was then successively extracted with solutions of ammonium carbonate, sodium carbonate, and sodium hydroxide. The ammonium carbonate removed only a small amount of resinous substance, from which nothing definite could be isolated. The sodium carbonate extract also consisted chiefly of resinous material, but by digesting the latter with alcohol, in which the resin was very soluble, a small amount (0·15 gram) of a crystalline substance was isolated. This substance, when recrystallised from dilute alcohol, separated in small, yellow needles, melting at 215—218°. Its solution gave a yellow colour with alkalis and with ferric chloride. With concentrated sulphuric acid it yielded an orange-red solution, slowly changing to pale yellow, but showing no fluorescence:

0·0816 gave 0·1904 CO_2 and 0·0290 H_2O. C=63·6; H=3·9.

$C_{16}H_{12}O_6$ requires C=64·0; H=4·0 per cent.

The *substance* thus appears to possess the formula $C_{16}H_{12}O_6$, but the amount available did not permit of its further characterisation. Although isomeric with the flavone derivatives, kaempferid (*Ber.*, 1881, **14**, 2385) and the luteolin monomethyl ether prepared synthetically by Diller and Kostanecki (*Ber.*, 1901, **34**, 1452), it is not identical with either of these compounds.

The sodium hydroxide extract of the above-mentioned ethereal liquid yielded on acidification a quantity (4·2 grams) of a crystalline substance, which, when recrystallised from alcohol, separated in glistening needles, melting at 207°. This substance was identified as the previously described casimiroic acid, which had evidently been formed by the action of the alkali on the lactone present in the ethereal liquid. After the successive extraction of the ethereal liquid with the above-mentioned alkalis, the solvent was evaporated, but only a slight, oily residue remained.

Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

The chloroform extract of the resin formed a hard, black mass, and amounted to 18·6 grams. The only crystalline substance obtained from it was a small quantity (0·6 gram) of the previously described alkaloid, casimiroine. The ethyl acetate and alcohol

extracts were dark-coloured products, and amounted to 3·2 and 22 grams respectively. Both of these extracts were heated with 5 per cent. sulphuric acid in aqueous alcohol, but they yielded nothing definite, although the aqueous liquid resulting from this treatment of the alcohol extract evidently contained some sugar, for it readily reduced Fehling's solution, and from the liquid, after the removal of the sulphuric acid, a little *d*-phenylglucosazone (m. p. 206°) was prepared.

II.—*Examination of the Shells.*

A small portion (10 grams) of the ground shells was subjected to a preliminary test for an alkaloid by digestion with Prollius' fluid. The reactions obtained were much less marked than in the case of the kernels, but indicated the presence of a small amount of alkaloidal substance.

Another portion (50 grams) of the ground material was successively extracted with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b.p. 35—50°)	extracted	0·2	gram =	0·4	per cent.
Ether	,,	0·3	,,	0·6	,,
Chloroform	,,	0·1	,,	0·2	,,
Ethyl acetate	,,	0·1	,,	0·2	,,
Alcohol	,,	0·8	,,	1·6	,,
	Total......	1·5	grams =	3·0	per cent.

For a complete examination of the shells a quantity (10·39 kilograms) of the ground material was completely extracted with hot alcohol. After the removal of the greater portion of the solvent, a thin extract, amounting to 482 grams, was obtained.

The whole of the above-mentioned extract was first distilled in a current of steam, when it yielded a very small amount (0·65 gram) of an essential oil. This oil appeared to be similar in character to that obtained from the kernels of the seed, but the amount was not sufficient for its further examination.

The aqueous liquid and resinous material remaining after the above-described treatment of the extract were examined by methods similar to those described in connexion with the kernels of the seed.

The chief constituents of the aqueous liquid were found to be amorphous colouring matter and sugar, the latter yielding *d*-phenylglucosazone, melting at 206°. No other crystalline product could be obtained from the liquid, the amount of alkaloidal substance present having proved to be too small to permit of its isolation.

The resinous material, when thoroughly washed and dried, formed a light brown, friable mass, and amounted to 95 grams, or about 0·9 per cent. of the weight of shells employed. The resin was

successively extracted with various solvents, and the resulting products separately examined. The petroleum extract, which amounted to 37 grams, contained a considerable quantity (20 grams) of stearic acid in a free state, together with a little free palmitic acid, and a small amount of these acids in the form of glycerides. The stearic acid, when crystallised from alcohol, separated in pearly leaflets, melting at 67—68°. (Found, C = 76·2; H = 13·1. Calc., C = 76·1; H = 12·7 per cent.) The ether, chloroform, ethyl acetate, and alcohol extracts of the resin amounted to 8·8, 30·4, 1·5, and 14·5 grams respectively, and consisted entirely of amorphous products. The chloroform and alcohol extracts were heated with 5 per cent. sulphuric acid in aqueous alcohol, but as they yielded no sugar by this treatment, they were not glucosidic in character.

Physiological Tests.

In order to ascertain whether either the hypnotic or toxic action attributed to *Casimiroa* seed (*loc. cit.*) could be confirmed, a number of tests were kindly conducted for us at the Wellcome Physiological Research Laboratories by Drs. H. H. Dale and P. P. Laidlaw, to whom our best thanks may here be expressed. All the products, with the exception of the essential oil, as noted below, were administered to dogs by the mouth.

The finely-divided kernel of an entire seed, weighing about 2 grams, as also 1 gram of the dry enzyme or protein material obtained from the seed, and representing 90 grams of the kernel, had no effect. One gram of the alcoholic extract, representing 3·2 grams of the kernels of the seed, produced vomiting and a temporary depression, which was apparently due to the repeated emesis, but no other effect could be observed. A similar effect was produced by the administration of 1 gram each of the petroleum and alcohol extracts of the resin, whereas the ether, chloroform, and ethyl acetate extracts of the resin were inactive. The following crystalline substances which had been isolated from the seed, namely, casimiroine, $C_{24}H_{20}O_8N_2$, casimiroedine, $C_{17}H_{24}O_5N_2$, and the lactone, casimirolid, $C_{24}H_{28}O_6$, were given to dogs in amounts of 0·4 gram, and also to cats in doses of 0·1 gram respectively, but the animals remained perfectly normal. Inasmuch as the experiments of Chevalier (*loc. cit.*) led him to conclude that the therapeutic value of *Casimiroa* seed is due to the essential oil or the resin which he presumed to be produced therefrom, a special test was conducted with the essential oil. A quantity (0·25 c.c.) of this product representing about 1100 grams of the kernels of the seed, when given to a cat, produced salivation and slight depression,

which may be ascribed to the nauseating taste of the substance, but there was no further effect, and particularly no trace of narcosis.

Summary.

The material employed for this investigation consisted of the fresh seeds of *Casimiroa edulis*, La Llave and Lejarza (Nat. Ord. *Rutaceae*), which were obtained directly from Mexico.

For the purpose of their examination, the kernels of the seed were first separated from the dry, fibrous shells. The latter, which represented about one-fifth the weight of the entire fresh seed, were separately examined, but yielded little of interest. They were found to contain a small amount of an essential oil, traces of alkaloidal substance, some sugar, and considerable stearic acid in the free state, together with resinous material.

The kernels of the seed, when subjected to a preliminary test, gave reactions indicating the presence of a considerable proportion of an alkaloid. They were also found to contain an enzyme, which was obtained in the form of a light brown powder, and slowly effected the hydrolysis of amygdalin.

An alcoholic extract of the ground kernels, when distilled in a current of steam, yielded a small amount of a pale yellow essential oil, which gradually darkened in colour. This oil had an agreeable, aromatic odour, and the following constants: $d = 0{\cdot}9574$ at 20°; $\alpha_D + 2°25'$ in a 25 mm. tube.

From the portion of the extract which was soluble in water there were isolated: (i) a new alkaloid, *casimiroine*, $C_{24}H_{20}O_8N_2$ (m. p. 196—197°), which is a very weak base, but yields a crystalline *picrate* (m. p. 165°) and an *aurichloride* (m. p. 195—196°). On heating casimiroine with alkalis, it undergoes hydrolysis, with the elimination of carbon dioxide, yielding a new base, *casimiroitine*, $C_{23}H_{22}O_7N_2$ (m. p. 171°), together with a small amount of a basic substance melting at 159°; (ii) a new alkaloid, *casimiroedine*, $C_{17}H_{24}O_5N_2$ (m. p. 222—223°; $[\alpha]_D$, in acid solution, $-36{\cdot}5°$), which yields a crystalline *aurichloride*; (iii) benzoic acid, with apparently a trace of salicylic acid. The aqueous liquid contained, furthermore, a quantity of sugar, which yielded *d*-phenylglucosazone (m. p. 205—207°).

The portion of the alcoholic extract which was insoluble in water consisted of a soft, oily resin. From this material the following compounds were isolated: (i) sitosterol, $C_{27}H_{46}O$ (m. p. 134—135°; $[\alpha]_D - 32{\cdot}1°$); (ii) ipuranol, $C_{23}H_{38}O_2(OH)_2$; (iii) a mixture of fatty acids, consisting of palmitic, stearic, oleic, linolic, and linolenic acids; (iv) a new lactone, *casimirolid*, $C_{24}H_{28}O_6$ (m. p. 229—230°; $[\alpha]_D - 49{\cdot}2°$), which yields a new hydroxy-acid, designated as

casimiroic acid, $C_{23}H_{28}O_4(OH)\cdot CO_2H$ (m. p. 207°; $[\alpha]_D - 86{\cdot}8°$). The following derivatives of this acid were prepared: *silver casimiroate*, $C_{23}H_{29}O_5\cdot CO_2Ag$; *methyl casimiroate*, $C_{23}H_{29}O_5\cdot CO_2CH_3$ (m. p. 108—110°); and *acetylcasimiroic acid*,

$$C_{23}H_{28}O_4(O\cdot COCH_3)\cdot CO_2H;$$

(v) a yellow, phenolic *substance*, $C_{16}H_{12}O_6$ (m. p. 215—218°).

It may finally be noted that the results of the present investigation of *Casimiroa* seed have afforded no evidence of the presence of a definite glucoside or a so-called "glucoalkaloid," as has previously been affirmed, and physiological tests conducted with animals have likewise failed to confirm their reputed hypnotic or toxic properties.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CCXXVII.—*Komppa's Synthesis of Camphoric Acid.*

By GUSTAVE LOUIS BLANC and JOCELYN FIELD THORPE.

THE publication of Komppa's reply to our criticism respecting his synthesis of camphoric acid (this vol., p. 29) has led us to investigate the action of very dilute alkali on methyl diketocamphorate (I). Under these conditions the compound is converted into the alkali salt of the dibasic acid, which eliminates carbon dioxide when acidified, and yields the monobasic acid (II). This substance passes into the diketone (III) when it is heated at 160°:

$$\underset{\text{(I.)}}{\left.\begin{array}{l}CO\cdot CMe(CO_2Me)\\ CO-CH(CO_2Me)\end{array}\right>CMe_2} \longrightarrow \underset{\substack{\text{(II.)}\\ \text{(M. p. 146°.)}}}{\left.\begin{array}{l}CO\text{——}CHMe\\ CO\cdot CH(CO_2H)\end{array}\right>CMe_2} \longrightarrow$$

$$\underset{\substack{\text{(III.)}\\ \text{(M. p. 83°.)}}}{\left.\begin{array}{l}CO\cdot CHMe\\ CO\text{—}CH_2\end{array}\right>CMe_2}$$

The lower homologue of this diketone (IV) is prepared by distilling methyl diketo*apo*camphorate with dilute sulphuric acid:

$$\left.\begin{array}{l}CO\cdot CH(CO_2Me)\\ CO\cdot CH(CO_2Me)\end{array}\right>CMe_2 \longrightarrow \underset{\substack{\text{(IV.)}\\ \text{(M. p. 45°.)}}}{\left.\begin{array}{l}CO\cdot CH_2\\ CO\cdot CH_2\end{array}\right>CMe_2}$$

The two diketones were characterised by the formation of the osazones and dioximes.

There is, then, no question that under the experimental conditions used by Komppa for the reduction of methyl diketocamphorate the methyl group remains attached to carbon; our criticism of his synthetical formation of camphoric acid is therefore baseless.

EXPERIMENTAL.

3 : 4-*Diketo*-1 : 1 : 2-*trimethyl*cyclo*pentane*-5(or 2)-*carboxylic Acid*,

$$\left.\begin{array}{l} CO\text{------}CHMe \\ CO\cdot CH(CO_2H) \end{array}\right> CMe_2 \quad \text{or} \quad \left.\begin{array}{l} CO\cdot CMe(CO_2H) \\ CO\text{--------}CH_2 \end{array}\right> CMe_2.$$

Five grams of methyl diketocamphorate were dissolved in a solution containing rather more than the theoretical amount of potassium hydroxide in ten times its weight of water, and allowed to remain at the ordinary temperature for twenty-four hours; the solution was then evaporated in a desiccator to half its volume, and acidified by hydrochloric acid. Carbon dioxide was eliminated, and the monobasic acid slowly separated; it was recrystallised from water at 50°, and obtained in small, flattened needles, melting at 146°, with immediate evolution of carbon dioxide:

0·2267 gave 0·4864 CO_2 and 0·1289 H_2O. C = 58·51; H = 6·37.

$C_9H_{12}O_4$ requires C = 58·7; H = 6·5 per cent.

3 : 4-*Diketo*-1 : 1 : 2-*trimethyl*cyclo*pentane*,

$$\left.\begin{array}{l} CO\cdot CHMe \\ CO\text{---}CH_2 \end{array}\right> CMe_2.$$

This diketone is formed when the above acid is heated in a bath of sulphuric acid at 160° until carbon dioxide ceases to be evolved. It crystallises from water containing a little alcohol in long, silky needles, which melt at 83°:

0·2098 gave 0·5260 CO_2 and 0·1620 H_2O. C = 68·42; H = 8·61.

$C_8H_{12}O_2$ requires C = 68·6; H = 8·6 per cent.

Like the similar compounds investigated by Dieckmann (*Ber.*, 1902, **35**, 3208), this substance is largely, if not entirely, enolic in structure; thus it gives a violet coloration with ferric chloride, and readily dissolves in aqueous potassium hydroxide, yielding a potassium salt, which is sparingly soluble in excess of alkali. It reacts, however, towards phenylhydrazine and hydroxylamine as a diketone.

The *osazone*, prepared in acetic acid solution, separates from alcohol containing a little water in small, yellow prisms, which melt at 162°:

0·1507 gave 22·1 c.c. of N_2 at 14° and 747 mm. N = 17·2.

$C_{20}H_{24}N_4$ requires N = 17·5 per cent.

The *dioxime* separates after some days from a solution of the ketone and hydroxylamine hydrochloride in dilute alcohol containing the theoretical amount of potassium hydroxide. It crystallises from dilute alcohol in long, slender needles, which melt and decompose at 172°:

0·1200 gave 0·2476 CO_2 and 0·0907 H_2O. C=56·32; H=8·21.

$C_8H_{14}O_2N_2$ requires C=56·3; H=8·4 per cent.

The diketone is soluble in water, and when pure can be recrystallised from this solvent; the aqueous solution is neutral to litmus. It completely sublimes at 70° without melting.

3:4-*Diketo*-1:1-*dimethyl*cyclo*pentane*,

$$\begin{array}{l} CO\cdot CH_2 \\ | \\ CO\cdot CH_2 \end{array}\!\!>CMe_2.$$

The preparation of this substance can be effected by boiling methyl diketo*apo*camphorate with dilute sulphuric acid (one of acid to three of water) for three hours, and distilling the product with steam. The diketone passes over as an oil, which boils at 197°/748 mm., and yields a distillate, which solidifies to a mass of needles on cooling. It melts at 45°, and is readily soluble in all organic solvents:

0·2279 gave 0·5541 CO_2 and 0·1591 H_2O. C=66·52; H=7·83.

$C_7H_{10}O_2$ requires C=66·7; H=7·9 per cent.

The *osazone*, prepared in acetic acid solution, separates as an oil, which resinifies on keeping. It can be obtained crystalline by rubbing with alcohol, and recrystallising from this solvent; it forms yellow needles, melting at 167°:

0·1355 gave 21·4 c.c. of N_2 at 16° and 746 mm. N=18·32.

$C_{19}H_{22}N_4$ requires N=18·3 per cent.

The enolic structure of this diketone is apparent from the fact that it gives a deep wine-red colour with ferric chloride, and dissolves in aqueous potassium hydroxide, yielding a solution from which excess of alkali precipitates the potassium salt in glistening plates. The potassium salt is readily soluble in water, and the solution deposits the diketone when acidified. The aqueous solution of the diketone is faintly acid to litmus.

THE SORBONNE,
PARIS.

THE SORBY RESEARCH LABORATORY,
THE UNIVERSITY, SHEFFIELD.

CCXXVIII.—*The Lower Limit of Inflammation of Mixtures of the Paraffin Hydrocarbons with Air.*

By MAURICE JOHN BURGESS and RICHARD VERNON WHEELER.

WHEN a source of heat, such as a lamp flame or an electric spark, is introduced into a mixture of a combustible gas and air, two things are necessary to ensure propagation of flame throughout that mixture.

Supposing that too small a proportion of combustible gas is present, only a small quantity of heat per unit volume of mixture is liberated when the layer surrounding the initial source of heat is inflamed, and the products of combustion have to impart heat to a considerable volume of "inert" gases. The number of collisions between molecules of combustible gas and of oxygen that are chemically fruitful is therefore small. Such collisions, resulting in combination, will occur only in the neighbourhood of the initial source of heat, around which an aureole or "cap" will form of a size dependent on the nature and quantity of the combustible gas present.

As the proportion of combustible gas is increased, a greater quantity of heat is evolved per unit volume of mixture, and a smaller volume of inert gases is present to absorb it; until a point is reached when the amount of heat contained in the products of combustion of any given layer is just sufficient to raise to its ignition-temperature * the layer adjacent. Flame is then propagated from layer to layer throughout the mixture without any necessity for the continued presence of the source of heat which started the inflammation, and the mixture is said to "inflame" or "explode" according to the rapidity of the propagation.

To ensure propagation of flame, therefore, it is necessary (1) that the initial source of heat should be of a volume, intensity, and duration sufficient to raise the layer of gases in its immediate vicinity to a temperature higher than, or as high as, the ignition-temperature of the mixture; and (2) that the heat contained in the products of combustion of this first layer should be sufficient to raise the adjacent layer to its ignition-temperature.

The smallest quantity of any combustible gas which, when mixed with a given quantity of air (or oxygen), will enable this self-propagation of flame to take place, is termed the *lower limit of inflammation* of the gas.

* By "ignition-temperature" we mean, accepting Nernst's definition, that temperature at which rapid self-heating of the mixture takes place.

Similarly, there is a *higher limit* of inflammation corresponding with the greatest quantity of inflammable gas, or, rather, with the smallest quantity of oxygen, that will allow self-propagation of flame. The experimental part of this paper deals only with the lower limit.

The first systematic determinations of the limits of inflammation were made in 1816 for "firedamp" by Davy, who thus describes them ("Collected Works," Vol. VI., p. 24): "When 1 part of firedamp was mixed with 1 of air, they burnt by the approach of a lighted taper, but did not explode; 2 of air and 3 of air to 1 of gas produced similar results. When 4 of air and 1 of gas were exposed to a lighted candle, the mixture being in the quantity of 6 or 7 cubical inches in a narrow-necked bottle, a flame descended through the mixture, but there was no noise; 1 part of gas inflamed with 6 parts of air in a similar bottle, produced a slight whistling sound; 1 part of gas with 9 parts of air, rather a louder sound; 1 part with 10, 11, 12, 13, and 14 parts, still inflamed, but the violence of combustion diminished. In 1 part of gas and 15 parts of air, the candle burnt without explosion with a greatly enlarged flame; and the effect of enlarging the flame, but in a gradually diminishing ratio, was produced as far as 30 parts of air to 1 of gas."

These experiments, therefore, place the lower limit of inflammation of the particular sample of "firedamp" that Davy used as between 6·3 and 6·7 per cent.

Davy's determinations were repeated in 1876 by Coquillon (*Compt. rend.*, 1876, **83**, 709), who ignited the mixture in a closed vessel by means of an electric spark. His results, and his description of them, are similar to Davy's, but he places the lower limit at about 5·8 per cent.

Later determinations of the limits of inflammation of "firedamp," and of a number of pure gases and vapours, have been made by Le Chatelier, in conjunction with Mallard (*Ann. des Mines*, 1883, 5) and Boudouard (*Compt. rend.*, 1898, **126**, 1344 and 1510). The figure given for firedamp (assumed to be pure methane) is 6·0 per cent. This figure has received general acceptance throughout the coal-mining world, to which it is, of course, of paramount importance.

The most recent results that have come to our notice are those published by Teclu (*J. pr. Chem.*, 1907, [ii], **75**, 212). Teclu states that the lower limit of inflammation of methane, prepared from sodium acetate, lies between 3·20 and 3·67 per cent.*

* Since this was written a letter from Dr. E. P. Perman has appeared in the correspondence columns of *Nature* (September 28th, 1911) entitled "Limits of

In connexion with the work on coal-dust explosions on which we have been engaged for the Mining Association of Great Britain, it was essential that we should know with certainty what was the smallest amount of firedamp which, when present in dust-free air at ordinary temperature and pressure, would enable flame to be propagated when a source of heat was introduced. Teclu's results differed so widely from those generally accepted that we found it necessary to make fresh determinations under conditions which would as far as possible eliminate sources of error such as cooling by the walls of the vessel in which the inflammable mixtures were ignited.

Moreover, we had reason to believe that "firedamp" should not be regarded as consisting of pure methane, or methane diluted with a greater or lesser quantity of air, but that in many samples other hydrocarbons are present in appreciable (and by no means negligible) quantities.

In this connexion Davy says (*loc. cit.*, p. 14): "Though all the specimens of firedamp which I have examined consisted of carburetted hydrogen mixed with different small percentages of carbonic acid and common air, yet some phenomena that I observed in the combustion of a blower induced me to believe that small quantities of olefient gas may be sometimes evolved in coal mines with the carburetted hydrogen."

A full discussion of the probable composition of firedamp as it exists in coal mines appears in a paper by Gray (*Trans. Inst. Mining Eng.*, 1910, **39**, 286), who points out that although methane is the only inflammable gas that has been reported as contained in firedamp in the large number of analyses that have been made in the last few years, yet since the proportion of firedamp in the atmosphere of a well-ventilated mine is usually small, it is quite likely that the relatively much smaller proportion of other inflammable gases has escaped recognition; and he places on record the analysis of a sample which contained noteworthy quantities of

Explosibility in Gaseous Mixtures." Dr. Perman states that he has obtained much wider limits than those usually given, and he gives for methane 2·5 per cent. as the lower limit of explosibility (inflammation) when mixed with air. Ignition was effected by means of an incandescent platinum wire, the experiments being carried out in a glass tube of about 10 c.c. capacity, having a stopcock at each end and a mercury gauge of small bore attached to the middle of the tube. Dr. Perman says: "when the explosion occurs the mercury moves more or less sharply, according to the force of the explosion, but a distinct movement, apart from that due merely to the expansion caused by the heating of the wire, can be seen with the proportions of gases given above." From the fact that a "distinct movement" of the mercury gauge could be observed, it does not necessarily follow that the mixture experimented with was explosive or even inflammable. The expansion caused by the heat of combustion of only a trace of inflammable gas would be sufficient to affect a sufficiently delicate gauge.

higher paraffins. If it is assumed that ethane was the only paraffin hydrocarbon present beside methane in this particular sample of firedamp, Gray's analysis shows that the combustible gas contained 55·5 per cent. of methane and 44·5 per cent. of ethane, the proportions present in the air mixture being 1·84 and 1·47 per cent. respectively.

Further, when it is remembered that the major portion of the inflammable gases that find their way into the ventilating current of coal mines issues from minute fissures in the coal,* and that the gases that can be extracted from coal at the ordinary temperature, either by exhaustion or by simply crushing, contain not only ethane but higher members of the paraffin series of hydrocarbons, it will be seen that the limits of inflammability of every sample of "firedamp" must not be regarded as identical with those of any one particular sample.

These considerations prompted us to determine the lower limit of inflammation of the higher members of the paraffin series of hydrocarbons when mixed with air, as well as that of methane. At the same time it appeared that it should be possible, by obtaining a sufficiency of data, to establish some definite relationship between the lower limit of inflammation of any gas and its known physical properties.

A "lower-limit mixture" is one such that a given volume must, under the conditions of its combustion, evolve just sufficient heat to raise an equal volume to its ignition-temperature. There are at least three factors which must obviously determine this necessary condition: (1) the calorific power of the gas; (2) the relative volume and specific heat of the diluent gases; and (3) the ignition-temperature of the mixture.

Of these three factors the first must undoubtedly exercise the preponderating influence; for, taking the paraffin series of hydrocarbons, C_nH_{2n+2}, when n is small the calorific value of the gas is much less than when n is large; so that, a priori, the higher the value of n the less volume of the gas need be present in air to form a lower-limit mixture. This means also that the higher the value of n the greater the volume of diluent gases present per unit volume of mixture. On the other hand, as is indicated by the determinations made by Dixon and Coward (Trans., 1909, **95**, 514), the

* Many investigations have been made regarding the nature of the gases that are contained in coal after it has been mined, when, presumably, considerable escape of gas has already occurred. Amongst the most important are those by von Meyer (*J. pr. Chem.*, 1872, [ii], **5**, 144, 407, **6**, 360), Thomas (*Journ. Chem. Soc.*, 1875, **28**, 793), and Bedson and McConnell (*Trans. Fed. Inst. Min. Eng.*, 1892, **3**, 307). More recently Porter and Ovitz (*U.S. Bureau of Mines, Tech. Paper*, 2, 1911) have conducted experiments with freshly-mined coal, and give some remarkable figures for the rate of escape of gases therefrom when crushed.

ignition-temperatures of the paraffin hydrocarbons appear to fall slightly as the series is ascended.

The effect of an increase in these two last-named factors is small in comparison with the effect of the increased calorific value of the gas, and they operate in a contrary direction.

As a first approximation, therefore, it would appear probable that the lower limit of inflammation should vary inversely as the calorific value of the gas; that is to say, if L = the proportion of the combustible gas necessary to form a lower limit mixture, and C = its calorific value,

$$L=f(1/C), \text{ or, say, } L=k1/C \quad . \quad . \quad . \quad . \quad (1),$$

where k is a constant, the meaning of which will be considered later. Before considering its probable meaning, it will be of interest to see to what extent equation (1) is borne out by our experimental numbers.

The value that we have obtained for the lower limit of inflammation of methane when mixed with air is 5·6.* That is to say, the lower-limit mixture contains 5·6 per cent. by volume of methane. The calorific value of methane is 189·1.† Substituting in equation (1) we obtain a value for k of 1059, and the relative values for L for other gases can then be calculated.

In the table that follows the relative values of L are calculated from equation (1) in this manner, using methane as the standard to obtain the value of k. The observed values of L were obtained for the pure gases in the manner described in the experimental part of this paper. In every case the mixtures were ignited in a closed spherical vessel when at atmospheric pressure, and saturated with moisture at the room temperature (20—25°). The values are expressed as volumes of the inflammable gas per hundred volumes of mixture. In a separate column are given the lower calorific values of the gases at constant volume expressed in large calories per gram-molecule:

Gas.	Calorific value.	L observed.		L calculated.
Methane	189·1	5·60	standard	5·60
Ethane	336·6	3·10		3·15
Propane	484·2	2·17		2·19
n-Butane	631·7	1·65		1·68
n-Pentane	779·2	1·37		1·36
*iso*Pentane	779·2	1·32		1·36

* Throughout this paper, unless otherwise stated, the numbers given for the lower limits of inflammation are expressed as percentages by volume of the mixture of the combustible gas with air, and refer to mixtures at atmospheric temperature and pressure.

† The value used in the *lower* value (Thomsen) expressed in large calories per gram-molecule.

The agreement between the observed and calculated values of L is very striking, and seems to point to a definite and dominating relationship between the calorific values of the gases named in the table—the paraffin hydrocarbons—and their lower limits of inflammation when mixed with air.

If, however, it is attempted to calculate the lower limit for gases other than the paraffin hydrocarbons in the same way, using methane as the standard to obtain the value of k, the results do not all agree with experiment; thus, hydrogen, for which Le Chatelier gives an experimental value 10·0 ("Leçons sur le Carbone," p. 266), should have a value 18·45 according to equation (1). There is, therefore, some other factor to be considered.

This becomes apparent also on attempting to calculate the theoretical quantities of gas that are necessary to obtain a lower-limit mixture, assuming the reaction on ignition to take place adiabatically.

If T = the temperature of ignition of the mixture;
t = the initial temperature;
c' = the specific heat at constant volume of air;
c'' = the specific heat at constant volume of the combustible gas;
x = the amount of combustible gas present by weight;
$100 - x$ = the amount of air present by weight;
Q = the heat evolved by one part by weight of the combustible gas;

then:

$$[(100-x)c' + xc''](T-t) = Qx,$$

or:

$$x = \frac{100c'(T-t)}{Q-(c''-c')(T-t)}.$$

The value of $(c''-c')(T-t)$ can be neglected compared with that of Q, being of the order of 1 part in 1000. So that, if $t=0$, the equation becomes:

$$x = \frac{100c'T}{Q} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

In attempting to use this equation for the calculation of the quantities of the paraffin hydrocarbons necessary, one is faced with the difficulty that their ignition-temperatures are very ill-defined; thus, Dixon and Coward (*loc. cit.*, p. 519) give the following figures for methane, ethane, and propane burning in oxygen:

Methane	between	556	and	700°
Ethane	,,	520	,,	630
Propane	,,	490	,,	570

and reference to the experimental part of their paper shows that in the case of all three gases peculiarities were noticed for which

no satisfactory explanation was offered. Their behaviour was, however, similar in many respects, and seemed to indicate an unduly prolonged period of slow, flameless combustion before ignition took place.

All things considered, the lower values seem to be the best to choose for the purpose of calculating the lower limits; for we wish to know the least amount of heat required.

For these three gases, the only members of the paraffin series of which Dixon and Coward have determined the ignition-temperatures, we have calculated the lower-limit values from equation (2), using the gram and the large calorie as units, and taking the specific heat of air at constant volume as 0·169.

Gas.	Percentage by weight required to form a lower-limit mixture.	Percentage by volume. Calculated.	Observed.
Methane	0·795	1·426	5·60
Ethane	0·783	0·754	3·10
Propane	0·753	0·495	2·17

That the calculated values should be smaller than the observed is easily explained by the fact that the reaction that takes place on ignition has been assumed to be adiabatic, whereas actually heat is bound to be communicated from the gases first inflamed, not only to the adjacent layer, but to layers at a further distance. The amount of heat transmitted in this way must be determined chiefly by the speed at which the flame is propagated; for the more rapidly each successive layer is raised to its ignition-temperature the less will be the quantity of heat dissipated throughout more distant layers or through the walls of the containing vessel. Further than this, a certain proportion of the energy liberated during the reaction appears as radiant energy, and is not imparted to the products of combustion as sensible heat.

In the case of the three paraffin hydrocarbons, methane, ethane, and propane, the observed quantities required to form lower-limit mixtures with air are about four times the calculated quantities. In the case of hydrogen, however, the calculated quantity is 5·92, whilst the observed (Le Chatelier) is 10·0; that is to say, only about one and three-quarter times as great. The factors, therefore, other than the calorific value of the gas, which determine the quantity necessary to form a lower-limit mixture, operate in a different degree in the case of the paraffin hydrocarbons from what they do in the case of hydrogen or, no doubt, other inflammable gases.

From the fact that for all the paraffin hydrocarbons experimented with these factors taken together assume a constant value [as shown by the close agreement of equation (1) with experiment], it would appear that the mechanism of combustion of the inflammable gas

plays an all-important part in determining the quantity necessary to form a lower-limit mixture. For in the case of the paraffins the chemical changes resulting in inflammation are of a similar nature, the result of the initial encounter between the molecules of hydrocarbon and oxygen being, in each case, the formation of an oxygenated molecule; thus Bone and Wheeler (Trans., 1902, **81**, 536; 1903, **83**, 1074) have shown that unstable intermediate products are formed during the slow combustion of methane, according to the following scheme of reaction:

1. $CH_4 + O_2 = H{\cdot}CHO + H_2O.$
   Formaldehyde.

2. (*a*) $H{\cdot}CHO + O_2 = CO_2 + H_2O.$
   (*b*) $2H{\cdot}CHO + O_2 = (2H{\cdot}CO_2H) = 2CO + 2H_2O.$

Similarly, in the case of ethane, Bone and Stockings (Trans., 1905, **87**, 1232) have shown that formaldehyde and acetaldehyde are formed as intermediate products during slow combustion (see also Bone and Drugman, Trans., 1906, **89**, 660).

In our experiments we have found that whenever the mixture contained less of the particular paraffin hydrocarbon used than was required to enable self-propagation of flame to take place, the water contained in the spherical explosion vessel gave an aldehydic reaction with Schiff's reagent; but that after a lower-limit mixture had been ignited no aldehydes could be detected. In the latter case the heat of reaction destroyed the aldehydes as soon as formed; in the former, where the flame burned only in the vicinity of the electric spark, the intermediate products of combustion had time to diffuse away to the cool parts of the containing vessel.

This mode of combustion "by stages" of the paraffins is to our mind a sufficient explanation of the difficulty that Dixon and Coward experienced in fixing a definite ignition-temperature for methane, ethane, and propane *; and it suggests a reason why, since their behaviour on oxidation is similar, the calorific value of the paraffins is the sole determining factor in calculating the relative lower limits of inflammation of mixtures of each with air.

Experimental.

The method of experiment that we have adopted has been that of passing an electric spark from an induction coil between ter-

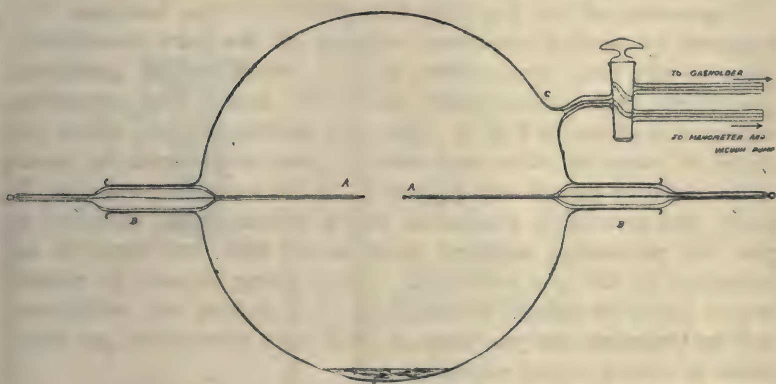
* Professor Dixon informs us that during the experiments made to obtain the ignition-temperatures of methane, ethane, and propane, a powerful odour of aldehyde was always noticed just before the gases inflamed, and that in some experiments the production of aldehyde seemed to be continued over a prolonged period at temperatures which in other experiments were sufficient to inflame the gases.

minals placed at the centre of the mixture of inflammable gas and air contained in a spherical vessel of about 2 litres capacity.

Previous workers have generally used an eudiometer tube of the diameter usually employed in the explosion analysis of gases; and have ignited the mixture either by passing an electric spark between platinum electrodes fused into the glass at one end of the tube, or by holding a lighted candle or taper to an open end of such a tube, the other end being closed. In either case the lower-limit mixture has been taken to be that in which the flame just travelled from one end of the tube to the other.

We considered that the cooling effect of the walls of such tubes may have influenced to some extent the results obtained, and therefore decided to use the spherical vessel above-mentioned, in

FIG. 1.



which the cooling by the walls would be reduced to a minimum. This method of experiment would also, it was thought, approximate more nearly to the conditions under which accidental ignitions of firedamp may take place in mines. We wished, moreover, to obtain some evidence of the influence, if any, of the size and intensity of the source of heat used to cause ignition, and of small variations in the initial temperature and pressure of the mixtures, on their lower-limit values.

The apparatus used is shown diagrammatically in Fig. 1. It consisted of a stout-walled glass globe nearly 16 cm. in diameter, with a capacity of just under 2 litres. The electrodes *A A*, which could reach to the centre, were platinum knobs, 3 mm. in diameter carried by stout platinum wires (coated with glass) along a diameter of the globe, passing by means of the parallel-ground joints, *B B*, through its walls. Each electrode, by reason of this

ground-glass connexion to the globe, could move horizontally through a distance of 3 cm., thereby allowing a maximum spark-gap of 6 cm. to be used. These "parallel" joints were made from accurately-ground hypodermic syringes, and, when lubricated with a solution of indiarubber in vaselin, maintained a vacuum during several hours.

Entrance to the globe was obtained through the tubulure *C*, to which was sealed a three-way tap of the form shown in the diagram. One branch of this tap made connexion with a glass gas-holder, in which the mixture to be experimented with was stored, and the other led to a mercury syphon manometer and a vacuum pump.

In all but a few special experiments a little distilled water (about 5 c.c.) was placed in the globe to saturate the mixture with water-vapour at the room temperature.

Preparation of the Gas and Air Mixtures.—The mixtures were prepared by adding measured volumes of the pure combustible gases to air, free from carbon dioxide, contained in graduated gas-holders over concentrated sulphuric acid. The apparatus employed is shown in Fig. 2. The pure combustible gas, which was stored in large test-tubes over mercury, was transferred, by means of the mercury trough and syphon, *A*, to the measuring cylinder, *B*, which was accurately graduated, and a volume taken sufficient to give the percentage required when mixed with four litres of air contained in the gas-holder, *C*. After being allowed to remain twelve hours to diffuse, a sample of the mixture was withdrawn and an explosion analysis made, a little pure electrolytic gas being added to ensure a good explosion.

The pure gases were prepared by the following methods:

Methane.—By the modification of Gladstone and Tribe's method described by Bone and Wheeler (Trans., 1902, **81**, 541). The gas was freed from traces of hydrogen by passage through "oxidised" palladium sponge heated to 98°, and by subsequent liquefaction by means of liquid air. The ratio C/A obtained in explosion analyses was exactly 2·0, showing that the gas was quite free from hydrogen.

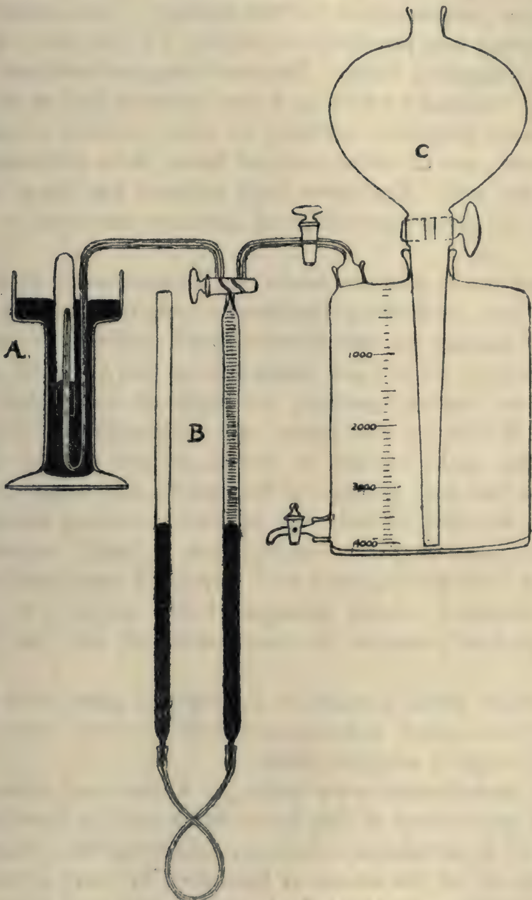
Ethane.—By the action of water on zinc ethyl. The gas was purified by several liquefactions with liquid air to remove traces of propane. The ratio C/A on explosion was 1·25 for one sample and 1·26 for another. (The ratio for pure ethane is 1·25.)

Propane and n-*Butane.*—By the action of nascent hydrogen (from zinc dust and dilute sulphuric acid) on the corresponding alkyl iodide. The gases were liquefied by cooling with solid carbon dioxide dissolved in ether, and fractionally distilled, the middle fraction only being collected. The sample of propane prepared

in this manner gave in an explosion analysis a ratio $C/A = 0{\cdot}99$; the sample of butane gave a ratio $= 0{\cdot}87$. (The ratios for pure propane and butane are 1·00 and 0·875 respectively.)

n-*Pentane and* iso*Pentane*.—The pure liquids were obtained from Kahlbaum, and a "stock" mixture of the vapour and air was

FIG. 2.



procured in each case by drawing dry air through the liquid contained in a wash-bottle maintained at 25°. In this manner mixtures containing high percentages of the hydrocarbon vapours were obtained; that of *n*-pentane and air containing 78·0 per cent. of *n*-pentane, and that of *iso*pentane and air containing 45·6 per cent. of *iso*pentane. The ratio C/A on explosion in the case of the

first-named was 0·81, and in the case of the second 0·80. (The ratio for pure pentane is 0·80.)

The pentane and air mixtures for the experiments were prepared from these stock mixtures by further dilution with air.

The manner of determining the lower-limit mixtures was that of "trial and error"; for example, a mixture of methane and air containing 6·1 per cent. of methane having been tried and found to propagate inflammation on the passage of an electric spark, a second mixture was prepared containing 5·9 per cent. of methane. This also propagated flame. The percentage of methane was therefore further reduced by 0·10 in a new mixture, and so on, until two mixtures were obtained, differing in their content of methane by 0·20 per cent., one of which enabled flame to be propagated, whilst the other did not. The lower-limit mixture was taken to be that containing the mean percentage of methane contained in these two mixtures.

The lower-limit mixture could be distinguished with certainty from that just containing insufficient combustible gas; for the momentary passage of the electric spark sufficed to promote the inflammation of all the gas contained in the globe in the former case, and on further sparking no signs of combustion could be observed. Whilst in the latter case, although the flame of the burning gas might appear to travel nearly through the whole mixture on the first passage of the spark, and some doubt might exist as to whether it had not, in fact, travelled throughout, on causing the spark to pass a second time, a "cap" appeared above it, showing that the mixture still contained combustible gas, and this cap remained whilst passage of the spark was continued, growing gradually smaller in size, until all the gas had been burnt.

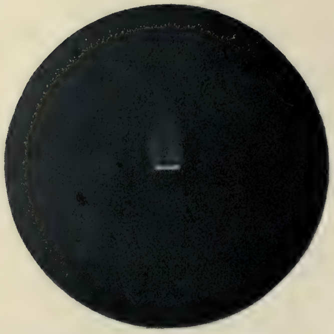
As a further check, samples of the residual gases were withdrawn from the globe after experiments with mixtures near the lower limit, and complete analyses made.

All the experiments were made in a darkened room, so as to enable the appearance of the flames to be readily observed.

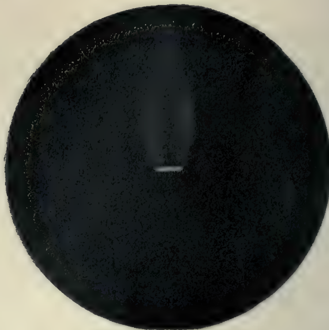
Results of Experiments.—Before considering the influence of the size and nature of the source of heat used to cause ignition, or the effect of variations in the initial temperature and pressure of the mixtures, we will give the details of the experiments made with the different gases when these conditions were constant.

For these experiments a spark-gap of 13 mm. was employed, the spark being obtained from a large induction coil. The initial pressure of the mixtures was between 760 and 765 mm., and the temperature between 20° and 25°. The gases were saturated with water-vapour at this temperature.

Fig. 3.



Methane, 4·30 per cent.



4·5 per cent.

4·65 per cent.

4·85 per cent.

5·00 per cent.

5·50 per cent.

[*To face p.* 2025.

Three, and sometimes four, experiments were made with the mixtures verging on the lower limit, the remainder being done in duplicate. The percentages of combustible gas recorded, determined by explosion analysis, are correct within 0·05; that is to say, for example, a mixture recorded as containing 4·30 per cent. of methane contained between 4·27 and 4·32 per cent.

Methane.

CH_4 present. Per cent. of mixture.	Effect of momentarily passing spark.	Effect of passing spark a second time.
4·30	Small flame or "cap" above spark, about 3 cm. high	Size of cap slightly diminished
4·50	Flame about 6 cm. high above spark	Size of cap slightly diminished
4·65	Flame about 8 cm. high spreading sideways above spark	Size of cap diminished
4·85	Large flame spreading through about a quarter of the mixture	Size of cap greatly diminished
5·00 and 5·25	Large flame spreading through about half the mixture	Size of cap greatly diminished
5·50	Distinct propagation, below the spark, of a blue flame which continued for a short time after the passage of the spark ceased	Small cap above spark about 1·5 cm. high. (A sample of the residual gases in the globe was found to contain about 3 per cent. of methane)
5·70	The flame travelled slowly throughout the mixture	No cap could be seen
5·80 and 5·90	The flame travelled throughout the mixture fairly quickly	No cap could be seen
6·10	The flame travelled rapidly throughout the mixture	No cap could be seen

The lower-limit mixture contains between 5·50 and 5·70 per cent. of methane.

Our results are in good agreement with those obtained by Coquillon and by Mallard and Le Chatelier, but are quite at variance with those obtained by Teclu. The effect of the spark on mixtures containing as much as 4·50 per cent. of methane makes it impossible for us to believe, as Teclu states, that mixtures containing 3·20 or 3·67 per cent. of methane can propagate flame under normal conditions as regards the initial temperature and pressure of the mixtures, and we conclude that either his method of analysis or his method of preparing the mixtures was faulty. In Fig. 3 are given diagrams representing the appearance of the flames in the different mixtures after the first passage of the electric spark, from which it will be seen that no doubt could exist regarding the inability to propagate flame of the mixtures containing a lower percentage of methane than 5·50. These diagrams show the appearance of the flame when it had attained its maximum dimensions.

The manner of movement of the flame in the 5·50 per cent. mixture suggested that if the gases were free to expand, ignition might possibly be propagated for a short distance. To test this, a different form of containing vessel was used, consisting of a vertical glass tube 3·5 cm. in diameter and 180 cm. long. The lower end of this tube expanded into a spherical chamber 10 cm. in diameter, in which platinum electrodes were fixed 20 mm. apart. The upper end of the tube could be closed by a ground-glass stopper.

The gaseous mixture, containing 5·50 per cent. of methane, was passed into the previously evacuated apparatus through a tap near the spherical end. An experiment was first made with the upper end of the tube closed by the glass stopper. On passing the electric spark, the flame of the burning gases filled the spherical chamber, and extended about 10 cm. upwards in the vertical tube. A second experiment was then made with a fresh supply of the same mixture. In this experiment, just before the spark was passed, the glass stopper was removed, leaving the upper end of the tube open to the outside air. The flame extended about 30 cm. up the vertical tube, and then died out.

Altogether, we are satisfied that the figure we give, 5·60, represents the smallest possible percentage of methane in a methane and air mixture that can enable self-propagation of flame to take place when the initial temperature and pressure of the mixture are atmospheric.

Ethane.

C_2H_6 present. Per cent. of mixture.	Effect of momentarily passing spark.	Effect of passing spark a second time.
2·40	A small flame above the spark, about 3 cm. high	Size of cap slightly diminished
2·70	Flame about 5 cm. high above spark	Size of cap slightly diminished
2·90 and 2·95	Large flame spreading through about one-third of the mixture	Size of cap greatly diminished
3·00	The flame travelled slowly through nearly the whole of the mixture	Small cap above the spark
3·20	The flame travelled fairly quickly throughout the mixture	No cap could be seen
3·35	The flame travelled rapidly throughout the mixture	No cap could be seen
3·50	The movement of the flame throughout the mixture could just be followed with the eye	No cap could be seen

The lower-limit mixture contains between 3·00 and 3·20 per cent. of ethane.

Propane.

C_3H_8 present. Per cent. of mixture.	Effect of momentarily passing spark.	Effect of passing spark a second time.
2·00	Small flame above spark about 6 cm. high	Size of cap diminished
2·10	Flame above spark spreading through about one-quarter of the mixture	Size of cap much diminished
2·15	Flame spreading nearly through the whole mixture	Small cap above spark
2·20	The flame spread slowly through the whole mixture	No cap could be seen
2·25	The flame moved fairly quickly through the mixture	No cap could be seen

The lower-limit mixture contains between 2·15 and 2·30 per cent. of propane.

n-*Butane.*

C_4H_{10} present. Per cent. of mixture.	Effect of momentarily passing spark.	Effect of passing spark a second time.
1·60	The flame reached the top of the globe and spread sideways through about one-third of the mixture	Small cap above spark
1·70	The flame travelled slowly through the whole mixture ; its movement could easily be followed with the eye	No cap could be seen
1·80	The flame travelled fairly quickly through the whole mixture	No cap could be seen

The lower-limit mixture contains between 1·60 and 1·70 per cent. of *n*-butane.

n-*Pentane.*

C_5H_{12} present. Per cent. of mixture.	Effect of momentarily passing spark.	Effect of passing spark a second time.
1·25	Flame above spark about 6 cm. high	Size of cap diminished
1·30	Flame above spark spreading through about one-third of the mixture	Size of cap much diminished
1·35	Flame above spark spreading through about half the mixture	Size of cap greatly diminished
1·40	The flame travelled slowly throughout the mixture	No cap could be seen
1·45	The whole of the gas burned fairly quickly	No cap could be seen

The lower-limit mixture contains between 1·35 and 1·40 per cent. of *n*-pentane.

iso*Pentane.*

C_5H_{12} present. Per cent. of mixture.	Effect of momentarily passing spark.	Effect of passing spark a second time.
0·90 and 1·20	Very small cap above spark	——
1·30	Flame above spark spreading through about one-third of the mixture	Small cap above spark
1·35	The flame travelled slowly throughout the mixture	No cap could be seen
1·40 and 1·45	The flame travelled fairly quickly throughout the mixture	No cap could be seen

The lower-limit mixture contains between 1·30 and 1·35 per cent. of *iso*pentane.

The Influence of the Size and Intensity of the Initial Source of Heat.—In discussing the influence of the volume of the initial source of heat on the propagation of flame in explosive mixtures of gases, Mallard and Le Chatelier put forward considerations (*loc. cit.*, p. 353), which can be paraphrased as follows: Assume that the source of heat is a sphere the temperature of which is higher than the ignition-temperature of the mixture. Before the molecules actually in contact with this sphere reach ignition-temperature, the surrounding molecules will have attained a certain temperature which will be lower the greater their distance from the heated sphere. The sphere, therefore, must communicate a certain quantity of heat to the surrounding gas before combustion can take place, without losing so much heat as to lower its temperature below the ignition-temperature of the mixture. The amount of heat communicated by the sphere in a given time is proportional to its radius squared (r^2), whilst the total quantity of heat that it contains is proportional to its radius cubed (r^3). It is obvious that the ratio between these two quantities, on which the propagation of inflammation depends, is proportional to the radius, that is to say, to the volume, of the sphere. This is found to be the case in actual experiment; a small electric spark of high temperature is insufficient to cause the inflammation of weak mixtures, which can, however, readily be ignited by the flame of a lamp—of less intensity than the electric spark, but of larger volume.

In the case of non-explosive mixtures, which contain a certain quantity of inflammable gas, but are unable to propagate flame, the introduction of a sphere the temperature of which is maintained above the ignition-temperature of the mixture will cause the combustion of the gas in a zone concentric with the sphere. The heat of combustion will increase the temperature of the surrounding mixture and automatically extend the radius of this zone. The sphere will thus be surrounded by a burning layer, the thickness

of which will be greater the higher the temperature of the sphere and the nearer the mixture approaches the lower-limit mixture.

It would appear, therefore, that above a certain limit, no increase in the size and intensity of the source of heat can affect the percentage of combustible gas that must be present to form a lower-limit mixture. The only effect that can follow an increase in the magnitude of the source of heat introduced into a mixture containing less combustible gas than is required to form a lower-limit mixture is an increase in the size of the aureole surrounding it.

We have made a number of experiments with mixtures of methane and air and ethane and air, in which the length of the spark from the induction coil was either 10, 15, 30, or 50 mm. The longest spark was no more effective than the shortest, and no great difference could be observed in the height of the cap formed.

Finally, by employing a Wehnelt electrolytic interrupter in circuit with the primary of the induction coil, using a current of 110 volts, we obtained a "flaming" spark, 30 mm. long, of large volume and great intensity. Comparative experiments were made with this source of ignition with most of the mixtures enumerated in the preceding tables. The results were, in general, as have been anticipated. The percentage of combustible gas required to form a lower-limit mixture suffered no reduction in consequence of the more violent means of ignition, but the size of the aureole surrounding the spark was greatly increased. Moreover, with mixtures that were capable of propagating flame, the flame appeared to travel more rapidly, and a greater pressure was momentarily produced than when the ordinary spark was used to cause ignition.

In illustration of the increase of the size of the aureole, the case of a mixture of ethane and air containing 2·45 per cent. of ethane may be mentioned. With the ordinary spark from the induction coil a cap about 3·5 cm. high appeared above the spark; with the Wehnelt spark the flame of the burning gases reached to the top of the globe and spread outwards through about one-third of the mixture.

The increased rapidity of combustion of inflammable mixtures is well shown in the case of a mixture of ethane and air containing 3·5 per cent. of ethane. When ignited by the ordinary spark the gases burned rapidly, but the movement of the flame could be followed with the eye; ignited by means of the Wehnelt spark, the mixture exploded violently, shattering the globe.

It has been suggested to us that the reason for this increased rapidity of combustion may lie in the great ionising power of the Wehnelt spark, and that, possibly, ionisation from an external source and ignition by means of an ordinary spark might produce

similar effects to the combined ignition and ionisation of the Wehnelt spark. We hope to be able to test this point.

The Influence of Small Variations in the Initial Temperature and Pressure of the Mixtures.—The experiments that we have made on the influence of the initial temperature and pressure of the mixtures in determining their lower-limit values have been confined to such small variations as may occur in coal-mining practise. That is to say, the highest temperatures and pressures that we have employed have been but little more than can exist in the deepest mine at present worked.

Such small variations in temperature and pressure do not appear to have any measurable influence on the lower-limit value of methane and air mixtures. With the initial temperature as high as 35°, and the pressure 800 mm., no self-propagation of flame could be observed with mixtures containing less than 5·60 per cent. of methane. On the other hand, with mixtures of ethane and air there seemed to be a tendency for mixtures containing slightly less than 3·10 per cent. of ethane to propagate flame when the initial pressure of the mixture was greater than 780 mm. and the Wehnelt spark was used; thus, in two experiments a mixture containing 3·00 per cent. of ethane propagated flame, the initial temperature being 24°. In another mixture, containing 2·95 per cent. of ethane, the flame only travelled through about two-thirds of the mixture.

We hope to be able to extend this work to a more complete study of the effect of pressure on the lower limit.

We wish to express our thanks to the Mining Association of Great Britain for permission to publish these results; and to the Explosions in Mines Committee of the Home Office for ratifying that permission.

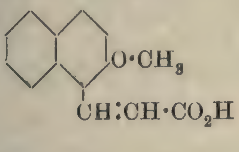
ALTOFTS.

CCXXIX.—*β-2-Methoxynaphthylpropionic Acid and Methoxy*peri*naphth-hydrindone.*

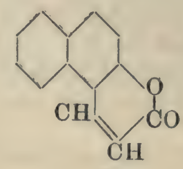
By GEORGE BARGER and WALTER WILLIAM STARLING.

A RECENT paper by Sachs and Brigl (*Ber.*, 1911, **44**, 2091) on ring-formation in the *peri*-position in the naphthalene series induces us to publish some experiments on the same subject which we made about a year ago, with but partial success. The method we wished to adopt was very similar to that which Sachs and Brigl had in view, namely, the removal of water from a naphthylacrylic or

propionic acid by a reaction like that used in the preparation of hydrindone. In order to prevent ring-formation by the removal of the hydrogen atom in position 2, we first replaced that hydrogen atom by a methoxy-group, and started therefore from 2-methoxy-naphthaldehyde. This was fairly readily converted into 2-methoxy-naphthylacrylic acid (I):

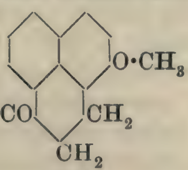


(I.)



(II.)

Sachs and Brigl, who employed the corresponding ethoxyaldehyde, were unable to bring about a similar condensation, and only obtained naphthacoumarin (II) by loss of the ethyl group. In our case this difficulty made itself felt in the next reaction (with phosphoric oxide), so that we likewise failed in our attempt to form a *peri*naphthindenone. When the naphthylacrylic acid was heated with excess of phosphoric oxide in benzene solution, no product could be isolated except a little of the naphthacoumarin (II), and this substance was also formed, in much larger quantity, when we heated the acrylic acid with one molecular proportion of phosphorus pentachloride. On the other hand, when we had reduced the naphthylacrylic acid to the corresponding propionic acid, its behaviour towards phosphoric oxide was changed, and we obtained a small quantity of a substance which we consider to be a *peri*naphth-hydrindone of the constitution III:



(III.)

The yields of methoxynaphthylpropionic acid and also of the above substance were so small that we were unable to prepare the corresponding phenol in order to submit it to distillation with zinc dust, as we had hoped to do.

Experimental.

Methylation of 2-Hydroxynaphthaldehyde.

Commercial hydroxynaphthaldehyde (from Schuchardt) and methyl sulphate were used. To 50 grams of the aldehyde, dissolved

in 440 c.c. of methyl alcohol, were added 28·6 c.c. of methyl sulphate, and then 27·4 c.c. of aqueous potassium hydroxide (11*N*). The addition of methyl sulphate and of potassium hydroxide was repeated twice. Each time a vigorous reaction should take place, and large quantities give a better yield than smaller ones. In the above experiment 43 grams of ether were obtained, and 10 grams of the hydroxyaldehyde were recovered. These were again methylated, so that the final yield amounted to 95 per cent. of the theory.

2-Methoxynaphthaldehyde is best purified by distillation; it boils at 205°/18 mm., and melts at 84°.

β-2-Methoxynaphthylacrylic Acid, $CH_3{\cdot}O{\cdot}C_{10}H_6{\cdot}CH{:}CH{\cdot}CO_2H$.

The above aldehyde did not react with sodium acetate and acetic anhydride, but it did with ethyl acetate and sodium. Ten grams of the aldehyde dissolved in 9·5 grams of ethyl acetate were treated with 1·25 grams of finely divided sodium (prepared by shaking under hot toluene). The resulting ester was hydrolysed on the water-bath with methyl-alcoholic sodium hydroxide, and yielded 11 grams of the crude acid, which separated from benzene and light petroleum in very pale yellow needles, melting at 160°:

0·1580 gave 0·4261 CO_2 and 0·0765 H_2O. C=73·55; H=5·4.

0·1286 was neutralised by 5·6 c.c. *N*/10-NaOH. M.W.=229.

$C_{14}H_{12}O_3$ requires C=73·7; H=5·3 per cent.; M.W.=228.

When the acid was heated on the water-bath in benzene solution with phosphoric oxide we could only isolate a minute quantity of a yellow, crystalline, neutral substance, which could not be purified completely, but was probably naphthacoumarin, first prepared by Kaufmann (*Ber.*, 1883, **16**, 686). The melting point was very indefinite, at about 80°, instead of 118°. By heating the same acid with one molecular proportion of phosphorus pentachloride on the water-bath, and distilling under diminished pressure, we obtained a 65 per cent. yield of a yellow substance, boiling at about 240°/12 mm. After crystallisation from benzene and light petroleum it melted at 117°, and was further identified with naphthacoumarin by analysis (Found, C=79·8; H=4·2. Calc., C=79·6; H=4·1 per cent.), and by the green fluorescence of its solution in concentrated sulphuric acid.

It is clear, therefore, that the methyl group was eliminated in the same way as the ethyl group in the experiments of Sachs and Brigl. The saturated acid, however, was found to react somewhat differently with phosphoric oxide, and in this case we obtained the desired *peri*naphth-hydrindone.

β-2-Methoxynaphthylpropionic Acid, $CH_3\cdot O\cdot C_{10}H_6\cdot CH_2\cdot CH_2\cdot CO_2H$.

The crude methoxynaphthylacrylic acid obtained from 20 grams of the aldehyde was reduced in sodium carbonate solution by 1 kilo. of 3 per cent. sodium amalgam, the solution being stirred by a motor. The mixture of acids which resulted was precipitated by hydrochloric acid, and extracted with several litres of boiling water, from which the saturated acid separated on cooling in colourless needles, melting at 128°. Yield, 2·6 grams:

0·2596 gave 0·6981 CO_2 and 0·1439 H_2O. C = 73·3; H = 6·1.

0·1500 was neutralised by 6·45 c.c. *N*/10-KOH. M.W. = 232.

$C_{14}H_{14}O_3$ requires C = 73·0; H = 6·1 per cent.; M.W. = 230.

The acid did not reduce potassium permanganate. It dissolved in about 1000 parts of boiling water.

*Methoxy*peri*naphth-hydrindone*, $C_{14}H_{12}O_2$.

With the small quantity of the last-named acid at our disposal we could only carry out a few experiments with phosphoric oxide. The most successful one was as follows: 1·3 grams of the acid were dissolved in 10 c.c. of benzene, and heated on the water-bath with 6·7 grams of phosphoric oxide for two to three hours. Powdered ice was then added to the reddish-violet reaction product, and after extraction with ether and washing with sodium carbonate, we obtained a small quantity of a yellow substance, which was distilled at 210°/12 mm., and then crystallised from benzene and light petroleum in deep yellow prisms, melting at 135°:

0·1344 gave 0 3897 CO_2 and 0·0583 H_2O. C = 79·1; H = 4·8.

$C_{14}H_{12}O_2$ requires C = 79·2; H = 5·6.

$C_{14}H_{10}O_2$,, C = 80·0; H = 4·8 per cent.

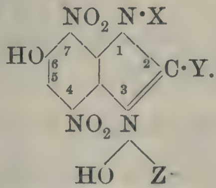
Of these two formulæ the first is by far the most likely. We satisfied ourselves that the methoxy-group was still intact, for on boiling with hydriodic acid, methyl iodide was evolved, but we had not enough material to repeat the analysis. We hope to find a better method of reducing methoxynaphthylacrylic acid in order to continue the experiments.

Chemical Laboratory, Goldsmiths' College,
New Cross, London, S.E.

CCXXX.—*Syntheses with Phenol Derivatives Containing a Mobile Nitro-group. Part V. Quinone-imides, Asymmetric Quaternary Ammonium Compounds, and Asymmetric Carbinols (continued).*

By Raphael Meldola and Harold Kuntzen.

The main object of the present extension of the research has been the study of the influence of the radicles X, Y, and Z in iminazolium compounds of the type:



on the general properties of these compounds, with a view to the selection of the most suitable types for the proposed investigation of the optical properties in the event of the bases or carbinols being resolvable. It was pointed out in our last paper (this vol., p. 1283) that the radicles in question were completely under control, and in the cases hitherto studied X has stood for phenyl and *p*-tolyl, and Z, excepting in one case, for methyl. In the present paper we describe other sets of compounds, in which X is represented by *p*-chlorophenyl, *p*-anisyl, and benzyl, Y and Z standing for methyl. Special attention has also been paid to the radicle Y attached to the 2-carbon atom, with a view to obtaining a series of homologues, and we have succeeded in preparing the compounds in which Y is represented by ethyl and *iso*butyl respectively, Z standing throughout this series for methyl, and X for phenyl. It is evident that there is scope for the indefinite extension of the research in the direction of synthesising new iminazoles and carbinols, but the fertility of the method has been sufficiently proved by the cases studied in this and the former papers, and it will be unnecessary to multiply instances, except for the elucidation of special points of theoretical interest. The general outcome of the experiments up to this point is to show that when the radicle X contains an acid substituent (Cl), the ammonium base forms salts of greater stability than when no such substituent is present. It appears also that with increase of weight in Y the general internal mobility also increases, so that in the higher homologues the conversion of the carbinol into the ammonium base takes place with extreme facility, a fact which

may be taken as proving that in this series the presence of hydroxyl in the benzene ring so influences the character of the molecule as to render the quinoneimide form the more stable. In this connexion it is of interest to recall the observations of Japp and Moir (Trans., 1900, **77**, 608), which indicate that in the case of the derivatives of lophine the carbinol form is the more stable, since the ammonium form passes readily into the latter.*

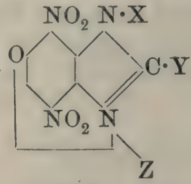
Further Theoretical Considerations.

The extension of the work since our last communication has led incidentally to the reconsideration of the theoretical interpretation of our results, and certain questions of considerable importance in relation to the formulæ proposed have necessarily arisen. As the result of our later work we see no reason for modifying the views advanced in our last paper, although there are certain assumptions upon which these views rest which require further verification. We propose calling attention to some of these points now, as much evidence will have to be accumulated before the questions raised can be satisfactorily settled. The question as to which of the two forms is the carbinol has already been dealt with (this vol., p. 1285). The evidence, as far as it goes, seems fairly conclusive, although the basic character of the isomeric iminazolium compound as evidence of the constitution of that form is to some extent weakened by the circumstance that the carbinols obtained by Otto Fischer are also basic (*J. pr. Chem.*, 1906, [ii], **73**, 422). It does not appear, however, from the researches of this author that the carbinols containing acid substituents in the benzene ring are likewise basic.

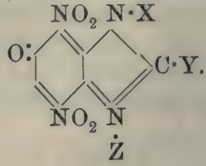
The argument from colour, although, as already pointed out (*loc. cit.*, p. 1286), subject to limitations, is, as far as it goes, in favour of the "quinoneimide" structure of the highly-coloured red form. The formula suggested for this modification on the strength of the evidence from colour, together with the chemical evidence already submitted, confessedly raises a difficulty which has led to the consideration of other possible formulæ for these coloured compounds. The formula in question (I) represents the quinonoid character, the relationship to the ammonium base, and the basic property of the molecule (see the general scheme in the last paper, *loc. cit.*, p. 1287), all of which characters are possessed by these red compounds. On the other hand, the alternative quinonoid formula (II) necessitates the assumption that a quinquevalent nitrogen atom

* The work of these authors furnishes a good example of the opening out of the iminazole ring, the ammonium hydroxide form of an amarine derivative passin spontaneously into the ethylenediamine derivatives.

can be in direct combination with carbon only, a state of combination hitherto unknown among quinquevalent nitrogen compounds. In answer to this objection it might be urged that the compounds

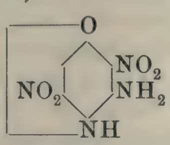


(I.)

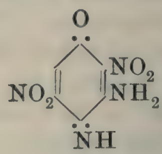


(II.)

are capable of existing in form I only, and not in the tautomeric form II. In other words, they may be regarded as derivatives of the hypothetical dinitroaminoquinoneimide (III), and not of its tautomeride (IV):



(III.)



(IV.)

Formula I represents the compound as the inner anhydride of the ammonium hydroxide derivative, and is in harmony with the fact that in some cases the transformation has been followed quantitatively by determining the actual loss of water on drying.* This formula does not violate any of the recognised canons of the constitution of the quinquevalent nitrogen compounds, as the fifth nitrogen bond is combined with the substituted acid phenyl nucleus. By this discussion there is thus raised the question of the possible existence of fixed quinonoid constitution, that is, of quinonoid compounds incapable of assuming the tautomeric (Fittig) form.

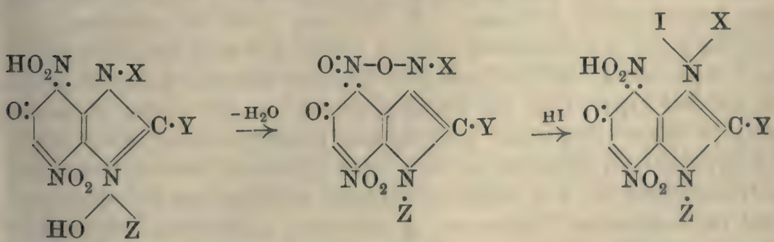
With respect to the possibility of quinquevalent nitrogen having all its bonds attached to carbon, it may be pointed out that groupings of the type $:\mathrm{C}{=}\dot{\mathrm{N}}{=}\mathrm{C}:$, in which both carbon atoms are contained in ring systems, have not hitherto been obtained so far as we are aware, so that no evidence from analogy appears to be available. In our compounds it will be noticed that one of the carbon atoms belongs to a ring highly charged with negative substituents, and may therefore be regarded as belonging to an *acid*

* It is only right to point out that in the majority of cases hitherto studied the ammonium hydroxide form could not be isolated, as it loses water readily, even on exposure to the air at the ordinary temperature, and passes into the anhydro-form. The extreme stability of these compounds when heated with concentrated sulphuric acid to the fuming point (this vol., p. 1294) is connected with the fact that it is the iminazolium sulphate which is being dealt with under these conditions.

radicle. From this point of view the proposed formula falls into line with compounds of the oxy-trialkylamine type.

Of other possible formulæ, that which represents the coloured compounds as having an ortho-quinonoid structure has received much consideration. The researches which have been carried out by Hantzsch and his colleagues during the few past years have made us familiar with the existence of the *iso*nitro-group (NO_2H) in compounds which had formerly been regarded as true nitro-derivatives, and reasons have already been given for suspecting such tautomerism in the original trinitroacetylaminophenol from which our iminazoles are prepared (Trans., 1910, **97**, 453). It is, in fact, possible, although we have no direct evidence to adduce in support of such a view, that the iminazoles themselves may be susceptible of such tautomerism:

In this connexion it is perhaps worth recalling attention to the fact that all our iminazoles are in the solid state or in solution of a pale ochreous colour, while their alkaline solutions and their solid salts are of an orange colour. Assuming, therefore, in accordance with the generally accepted view (Pinnow and Sämann, *Ber.*, 1899, **32**, 2181; Japp and Moir, Trans., 1900, **77**, 614) that when in a ring system an atom of nitrogen becomes quinquevalent, it is preferentially that atom which is associated with the double linking, the methiodide and corresponding ammonium base might be formulated on the above hypothesis as quinonoid compounds (I), anhydridisation taking place with rearrangement of internal linking between the 3-hydroxyl group and the 7-*iso*nitro-group. The product would then be an "inner" salt of the nitroic acid type, and would have an ortho-quinonoid structure (II):

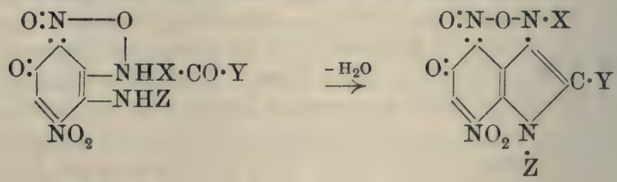


(I.) (II.) (III.)

This hypothesis is certainly worthy of being kept in view, although the balance of evidence seems to us to be against it. Some

of the objections to the proposed alternative scheme are worthy of record in view of their being met by further experimental evidence. In the first place, anhydridisation between hydroxyl groups in the meta-position is less probable than between such groups in the para-position, as is assumed in our original hypothesis. In the next place the formation of salts (iodides) by combining the quinonoid compounds (II) with acids would lead to the production of compounds isomeric with the original methiodide (III), unless we assume that there is another rearrangement of internal linking and the reconversion of the 3*N*-atom into the quinquevalent form. This is, of course, a possibility, but it introduces unnecessary complication into the chemical mechanism, and, as a fact, no such isomerism has hitherto been observed, the iodide obtained by combining the quinoneimide with hydriodic acid being apparently identical with the methiodide obtained by direct methylation of the iminazole (this vol., p. 1296).

The objection to the supposition that anhydridisation can take place between hydroxyl groups in the meta-position might perhaps be met by assuming that the hydrolysis of the methiodide results in the opening out of the iminazole ring with the formation of an intermediate ortho-diamine derivative, which, on this supposition, would be an inner salt of the nitroic acid type (I):



(I.) (II.)

The latter might then be supposed to anhydridise in the usual way with the formation of the ortho-quinonoid compound (II). This view, which, as we learn from a private communication, has also suggested itself to Dr. James Moir, is, however, at variance with the experimental evidence. In no case have we observed any tendency for the iminazole ring to break down in our compounds, and experiments directed specially towards this end have, as shown in our last paper, thus far led to negative results. If the iminazole ring in these compounds were so easily broken down, they might be expected, in accordance with Otto Fischer's results, to furnish nitrosoamines by the action of nitrous acid, azines by oxidation, and ortho-diamine derivatives by complete hydrolysis. No one of these properties is possessed by our compounds. A crucial test of the validity of the ortho-quinonoid formula would be the formation of analogous compounds containing some substituent other

than a nitro-group in position 7. Experiments having for their object the synthesis of iminazoles containing a halogen atom in this position have been commenced, but we have not yet succeeded in preparing compounds of this type; this branch of the work has, however, only been tentatively dealt with at present.

So far as concerns the formation of the carbinol from the ammonium compound, either the ortho- or the para-quinonoid formula will represent the transformation. The balance of evidence is, however, thus far so distinctly in favour of the latter that we see no reason for departing from our original view of the constitution of these compounds.

Experimental.

In order to condense the descriptive details of the work as much as possible, each set of compounds is dealt with under the heading indicating the iminazole used as the starting point. In all cases the methiodide was first prepared.

The Iminazole from Trinitroacetylaminophenol and p-*Anisidine.*

The iminazole (Meldola and Hay, Trans., 1908, **93**, 1675) was converted into the iminazolium iodide by heating with excess of methyl iodide for three hours at 125°. The iodide, which consists of small, ochreous needles, is slowly decomposed by boiling with water, but more rapidly by boiling with dilute hydrochloric acid. On neutralising the hot acid solution with ammonia, the iminazolium compound separates out on cooling as a brick-red, microcrystalline powder. The air-dried substance proved on analysis to be the quinoneimide, 4:7-*dinitro*-1-p-*anisyl*-2:3-*dimethyl*-6-*benziminazolone,* a fact indicating that anhydridisation takes place very readily in this case, possibly in the hot aqueous solution:

0·0986 gave 13·7 c.c. N_2 (moist) at 21·5° and 759·9 mm. N=15·77.

$C_{16}H_{14}O_6N_4$ requires N=15·66 per cent.

The substance is extremely basic, dissolving readily in dilute acids with the formation of salts which are stable only in presence of excess of acid. The hydrochloride (4:7-*dinitro*-6-*hydroxy*-1-p-*anisyl*-2:3-*dimethylbenziminazolium chloride*) was prepared by the action of a saturated alcoholic solution of hydrogen chloride on the foregoing compound. It consists of small, white needles, easily dissociable by water:

0·0968 gave 0·0351 AgCl. Cl=8·96.

0·0858 „ 10·5 c.c. N_2 (moist) at 21·5° and 763 mm. N=13·95.

$C_{16}H_{15}O_6N_4Cl$ requires Cl=8·98; N=14·2 per cent.

The carbinol, 4 : 7 - *dinitro* - 6 - *hydroxy*-1-p-*anisyl*-2 : 3-*dimethyl*-2-*benziminazolol*, was prepared by dissolving the iminazolone in warm dilute sodium hydroxide, and precipitating by hydrochloric acid. The compound separates as a microcrystalline, ochreous powder, which passes readily into the red iminazolone on heating, the conversion taking place in a few minutes on boiling with alcohol or water, and also slowly on drying the solid at 100°. The best analytical results were for this reason given by the air-dried substance:

0·1016 gave 13·2 c.c. N_2 (moist) at 19° and 771·5 mm. N = 15·17.

$C_{16}H_{16}O_7N_4$ requires N = 14·89 per cent.

The Iminazole from Trinitroacetylaminophenyl and p-*Chloroaniline.*

The iminazole (m. p. 246°; Meldola and Hay, Trans., 1908, **93**, 1676) had to be heated with excess of methyl iodide to 130° for two to three hours to bring about complete transformation into the methiodide. The latter is a crystalline substance, consisting of dark ochreous scales. Decomposition was effected by boiling with dilute hydrochloric acid, the iminazolone being precipitated from the acid solution on adding ammonia in slight excess. This compound crystallises in small, ochreous scales, which do not decompose at 300°. An air-dried specimen was used for analysis:

0·0832 gave 11·5 c.c. N_2 (moist) at 20° and 759·5 mm. N = 15·8.
0·1088 ,, 0·0420 AgCl. Cl = 9·54.

$C_{15}H_{11}O_5N_4Cl$ requires N = 15·45; Cl = 9·77 per cent.

This compound (4 : 7-*dinitro*-1-p-*chlorophenyl* - 2 : 3 - *dimethyl*-6-*benziminazolone*) is characterised by the stability of its hydrochloride, which is not completely dissociated by excess of hot water. It is for this reason that excess of ammonia is required for the precipitation of the pure iminazolone from its acid solution. The salt (4 : 7-*dinitro*-6-*hydroxy*-1-p-*chlorophenyl*-2 : 3-*dimethylbenziminazolium chloride*) was prepared by dissolving the iminazolone in hot 50 per cent. hydrochloric acid, filtering, and allowing to cool, when the compound separated as a white, microcrystalline powder, which was collected, washed with a little cold water, and allowed to dry in the air:

0·2012 gave 24·4 c.c. N_2 (moist) at 17° and 761·5 mm. N = 14·10.
0·1627 ,, (on decomposition by an alcoholic solution of silver nitrate) 0·0572 AgCl. Cl = 8·70.

$C_{15}H_{12}O_5N_4Cl_2$ requires N = 14·04; Cl (1 atom) = 8·88 per cent.

The carbinol, 4 : 7-*dinitro*-6-*hydroxy*-1-p-*chlorophenyl*-2 : 3-*dimethyl*-2-*benziminazolol*, was prepared in the usual way by dissolving the iminazolone in alkali, and precipitating by acid. It consists of an

ochreous, non-basic, microcrystalline powder, which is converted into the basic iminazolone on boiling with alcohol or water:

0·0976 gave 12·8 c.c. N_2 (moist) at 21° and 760·1 mm. N=14·93.
$C_{15}H_{13}O_6N_4Cl$ requires N=14·72 per cent.

It will be noted that in this case, as in that of the *p*-tolyl compound (this vol., p. 1286), the iminazolone and carbinol do not differ markedly in colour.

The Iminazole from Trinitropropionylaminophenol and Aniline.

After numerous experiments having for their object the preparation of iminazoles having radicles other than methyl attached to the 2-carbon atom, it was found that the most satisfactory results were obtained by acylating the trinitroaminophenol prepared by the hydrolysis of its acetyl derivative (Meldola and Hay, Trans., 1909, **95**, 1378). For the present series the dry trinitroaminophenol was heated for some time on the water-bath with excess of propionic anhydride, the product diluted with water, and the solid propionyl compound purified by crystallisation from glacial acetic acid.

2:3:5-*Trinitro-4-propionylaminophenol* crystallises from acetic acid in nodular aggregates of opaque, ochreous needles, melting at 178—179°:

0·0915 gave 15·1 c.c. N_2 (moist) at 21·5° and 760·7 mm. N=18·76.
$C_9H_8O_8N_4$ requires N=18·67 per cent.

4:7-*Dinitro-6-hydroxy-1-phenyl-2-ethylbenziminazole* was prepared from the above trinitro-compound by boiling it in alcoholic solution with aniline according to the method described in former papers. The product after crystallisation from alcohol with the addition of animal charcoal was obtained in ochreous, transparent, rhombohedral plates, becoming opaque at 100°, and melting at 173°:

0·1666 gave 24·5 c.c. N_2 (moist) at 17·5° and 760·7 mm. N=17·04.
$C_{15}H_{12}O_5N_4$ requires N=17·08 per cent.

4:7-*Dinitro-6-hydroxy-1-phenyl-2-ethyl-3-methylbenziminazolium iodide* was prepared by heating the iminazole with excess of methyl iodide to 120° for three hours. The product consisted of small, reddish-brown scales, the analysis of which indicated that the formation of the methiodide was practically complete:

0·1814 gave 18·3 c.c. N_2 (moist) at 18·7° and 755·7 mm. N=11·54.
$C_{16}H_{15}O_5N_4I$ requires N=11·92 per cent.

4:7-*Dinitro-1-phenyl-3-methyl-2-ethyl-6-benziminazolone* was obtained from the iminazolium iodide by boiling the latter with dilute hydrochloric acid, and neutralising the filtrate with ammonia. After

being twice treated in this way, the pure compound was obtained in small, brick-red scales, decomposing above 300°:

0·0978 gave 13·9 c.c. N_2 (moist) at 21·5° and 774·4 mm. N=16·45.
$C_{16}H_{14}O_5N_4$ requires N=16·47 per cent.

4:7-*Dinitro-6-hydroxy-1-phenyl-2-ethyl-3-methylbenziminazolium chloride* was prepared from the iminazolone by treating the latter in the cold with an alcoholic solution of hydrogen chloride. It crystallises in white granules, easily dissociable by water:

0·1500 gave 19·3 c.c. N_2 (moist) at 23° and 772 mm. N=14·66.
0·2258 „ 0·0829 AgCl. Cl=9·08.
$C_{16}H_{15}O_5N_4Cl$ requires N=14·8; Cl=9·36 per cent.

The carbinol, 4:7-*dinitro-6-hydroxy-1-phenyl-3-methyl-2-ethyl-2-benziminazolol*, was prepared in the usual way by the action of dilute sodium hydroxide on the iminazolone, and precipitation by acid. It crystallises in microscopic, ochreous needles, which pass very readily into the red iminazolone on boiling with water or alcohol or on heating in the dry state:

0·0833 gave 0·1632 CO_2 and 0·0326 H_2O. C=53·43; H=4·35.
0·0786 „ 11·1 c.c. N_2 (moist) at 25° and 764·6 mm. N=15·85.
$C_{16}H_{16}O_6N_4$ requires C=53·3; H=4·48; N=15·55 per cent.

*The Iminazole from Trinitro*isovaleryl*aminophenol and Aniline.*

Attempts to prepare trinitro*iso*valerylaminophenyl by first introducing one or two valeryl groups into *p*-aminophenol and then nitrating the product under various conditions, showed that this method was unsatisfactory. The divaleryl compound is easily prepared by the action of valeric anhydride on *p*-aminophenol in the presence of a few drops of sulphuric acid, but the product is viscous and uncrystallisable. It can be nitrated in cooled glacial acetic acid by means of fuming nitric acid, and yields a *dinitro*-derivative, which crystallises in flat, ochreous needles, melting at 177°. The *O*-valeryl group is eliminated during nitration as the product is phenolic, and has the composition of a *dinitromonovaleryl-*p*-aminophenol*:

0·1186 gave 15·05 c.c. N_2 (moist) at 14° and 768·2 mm. N=15·09.
$C_{11}H_{13}O_6N_3$ requires N=14·84 per cent.

This dinitro-compound could not be readily converted into a trinitro-compound, so the method was abandoned, and the alternative process of acylating trinitroaminophenol adopted.

2:3:5-*Trinitro-1:4-di*iso*valerylaminophenol* was prepared by the action of excess of *iso*valeric anhydride on *p*-aminophenol. In the presence of sulphuric acid acylation takes place readily at the

ordinary temperature in the course of a few hours; without sulphuric acid acylation takes place readily on warming on the water-bath for about an hour. In both cases the divaleryl compound is produced, the latter crystallising from alcohol in pale yellow needles, melting at 119°:

0·0770 gave 9 c.c. N_2 (moist) at 16° and 762·7 mm. N=13·68.

$C_{16}H_{20}O_9N_4$ requires N=13·59 per cent.

4:7-*Dinitro*-6-*hydroxy*-1-*phenyl*-2-iso*butylbenziminazole* was prepared by heating the foregoing compound with excess of aniline in alcoholic solution in the usual way. After purification by alkaline treatment and crystallisation from alcohol, it consists of ochreous scales, melting at 156°:

0·1712 gave 0·3602 CO_2 and 0·0778 H_2O. C=57·39; H=5·04.

0·1330 „ 18·2 c.c. N_2 (moist) at 20° and 759·4 mm. N=15·63.

$C_{17}H_{16}O_5N_4$ requires C=57·27; H=4·52; N=15·73 per cent.

It is of interest to note that during the formation of this iminazole, the *O-iso*valeryl group is eliminated, and that *iso*valeranilide is found among the products left after the process of purification by alkaline extraction.

4:7-*Dinitro*-6-*hydroxy*-1-*phenyl*-2-iso*butyl*-3-*methylbenziminazolium iodide* was prepared by heating the iminazole in a sealed tube with excess of methyl iodide for three hours at 120°. The methylation appeared to be very complete, the methiodide crystallising in orange-red needles. Decomposition of the methiodide was readily effected by boiling the crystalline compound with dilute hydrochloric acid, in which it freely dissolves, filtering the solution, and neutralising with ammonia, when the iminazolium base is precipitated as an orange, microcrystalline powder. In order to insure complete decomposition of the methiodide, the treatment with dilute hydrochloric acid was repeated.

4:7-*Dinitro*-1-*phenyl*-3-*methyl*-2-iso*butyl*-6-*benziminazolone* is a substance of distinctly basic character, dissolving readily in all mineral acids, and being precipitated unchanged on neutralising the acid solution with ammonia. The decomposing point is above 300°. The compound may exist in the ammonium hydroxide form when freshly precipitated, but it loses water on drying in the air at the ordinary temperature, and passes into the quinoneimide:

0·1148 gave 15·5 c.c. N_2 (moist) at 22° and 772·6 mm. N=15·55.

$C_{18}H_{18}O_5N_4$ requires N=15·13 per cent.

The *iminazolium chloride* is formed from the quinoneimide by the action of an alcoholic solution of hydrogen chloride, from which solvent it separates in small, white needles, readily dissociable by water with the regeneration of the quinoneimide:

0·1286, decomposed in alcoholic solution with silver nitrate, gave 0·0455 AgCl. Cl = 8·74.

$C_{18}H_{19}O_5N_4Cl$ requires Cl = 8·71 per cent.

The carbinol, 4 : 7-*dinitro*-6-*hydroxy*-1-*phenyl*-3-*methyl*-2-iso*butyl*-2-*benziminazolol*, was prepared in the usual way by dissolving the quinoneimide in warm dilute sodium hydroxide, and precipitating by hydrochloric acid. It crystallises in small, ochreous needles, which pass with extreme readiness into the ammonium form, a few minutes' boiling with water or alcohol being sufficient to convert the phenolic carbinol into the basic ammonium compound. The specimen used for analysis was dried in the air at the ordinary temperature, as heating in the water-oven brings about partial dehydration owing to the formation of the quinoneimide:

0·1263 gave 16·3 c.c. N_2 (moist) at 22·5° and 757·2 mm. N = 14·52.
0·1182 „ 0·2404 CO_2 and 0·0522 H_2O. C = 55·47; H = 4·91.
$C_{18}H_{20}O_6N_4$ requires C = 55·64; H = 5·19; N = 14·43 per cent.

The Iminazole from Trinitroacetylaminophenol and Benzylamine.

The iminazole (Trans., 1906, **89**, 1940) was methylated by heating with excess of methyl iodide for two hours at 120°. The methiodide consisted of red, ochreous scales, which required prolonged boiling with water in order to effect conversion into the iminazolium compound, the latter crystallising from the solution on cooling in bright red needles, melting and decomposing at 252—253°. Analyses of the air-dried substance showed that dehydration had taken place with the formation of the iminazolone, 4 : 7-*dinitro*-1-*benzyl*-2 : 3-*dimethyl*-6-*benziminazolone*:

0·0638 gave 8·9 c.c. N_2 (moist) at 12·5° and 751·3 mm. N = 16·33.
$C_{16}H_{14}O_5N_4$ requires N = 16·37 per cent.

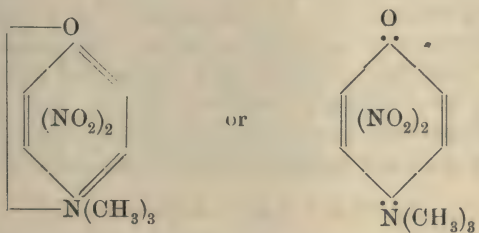
The *iminazolium chloride* was prepared by dissolving the iminazolone in alcoholic hydrochloric acid and adding ether; the salt separates as a pale, ochreous, microcrystalline powder, having when dry a melting point of 218°:

0·0638 gave 8·1 c.c. N_2 (moist) at 14° and 764·5 mm. N = 15·02.
0·1328 „ (by the method of Carius) 0·0501 AgCl. Cl = 9·32.
$C_{16}H_{15}O_5N_4Cl$ requires N = 14·8; Cl = 9·36 per cent.

The salt used for analysis was air-dried, as it dissociates on heating, and also rapidly in contact with water, the red iminazolone being regenerated. We have been unable to prepare the carbinol form of this compound owing to the extreme difficulty of realising the precise conditions necessary in order to ensure successful conversion of the iminazole into the iminazolium iodide. Numerous

experiments have been made under various conditions, but the results have so far been unsatisfactory. As the completion of this series is not of immediate importance, this part of the research has for the present been abandoned.

We desire, in concluding, to express our indebtedness to the Government Grant Fund of the Royal Society for material assistance towards the expenses of the research. We have also much pleasure in acknowledging the valuable co-operation of Mr. William F. Hollely, who has taken a considerable part in the experimental work. We may point out also that while the foregoing results were being prepared for publication, another research being carried out in our laboratory has led to the unexpected discovery of independent confirmation of the existence of quinoneimidonium compounds of the type:



in which quinquevalent nitrogen is combined with three alkyl groups and a carbon atom belonging to the strongly acid quinonoid radicle $[C_6H_2(NO_2)_2O]^{II\text{ or }IV}$, and therefore ascribable to the type of the oxytrialkyl or mixed ammonium compounds, $O\colon N(Alk)_3$, $O\colon N(Alk)_2Ar$, etc. This discovery has arisen from the further study of the product of the extreme methylation of *iso*picramic acid described in a preliminary note by one of the authors published last year (Proc., 1910, **26**, 232). This research is in progress, and the results will be communicated to the Society when sufficiently mature.

City and Guilds of London Technical College,
Finsbury.

CCXXXI.—*The Synthesis of Derivatives of Thioxanthone. Part IV. Synthesis from Aromatic Sulphinic Acids.*

By Harold Christopher and Samuel Smiles.

In previous communications it has been shown that various types of thioxanthone derivatives may be synthesised from aromatic mercaptans (Trans., 1910, **97**, 1290), from aromatic disulphides (this vol., p. 1353), and from the products obtained by the union of a quinone with *o*-thiolbenzoic acid (this vol., p. 1535). In the two former methods the union of the thio-derivative with the aromatic compound is effected by the condensation of a sulphoxylic acid which is formed at an intermediate stage in the process, water being eliminated from this substance and the second aromatic nucleus. Since it has been formerly observed (Smiles and Le Rossignol, Trans., 1906, **89**, 700) that aromatic sulphinic acids readily condense with suitable aromatic compounds in the presence of sulphuric acid:

$$Ar{\cdot}SO_2H + HAr' = ArSOAr' + H_2O,$$

the present experiments were undertaken in order to apply this type of interaction to the production of thioxanthones.

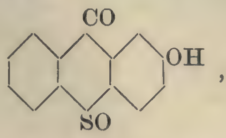
Both Graebe (*Annalen*, 1891, **263**, 1) and Mayer (*Ber.*, 1909, **42**, 1134, 3046) have shown how easily thioxanthones are formed by elimination of water from the *o*-carboxylic derivatives of substituted diphenyl sulphides:

$$C_6H_4{<}^{CO_2H}_{S\text{———}}{\diagup}C_6H_5 = H_2O + C_6H_4{<}^{CO}_{-S-}{>}C_6H_4,$$

so that the synthesis of thioxanthones by this method is merely a question of choosing suitable aromatic derivatives for condensation with the sulphinic acid. This condensation takes place most readily with hydroxy- and amino-derivatives of benzene, and, since the quadrivalent sulphur grouping then enters the para-position (Smiles and Le Rossignol, *loc. cit.*) with respect to these groups, the *m*-hydroxy- and amino-benzoic acids have been employed in these experiments.

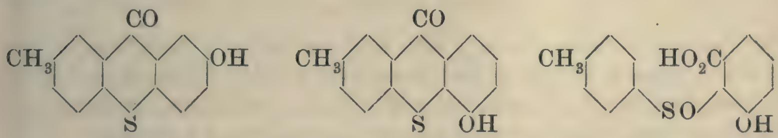
Two methods of effecting the condensation have been investigated, either with warm sulphuric acid or by the aid of heat alone (see Hinsberg, *Ber.*, 1903, **36**, 107); but since the former agent furnishes very poor yields, the latter has been generally adopted. It might be expected that the product furnished by either process would

not be the thioxanthone, but instead the oxide thereof, for example,



but this is not the case, for it appears that at the relatively high temperatures employed the sulphoxide is easily reduced to the sulphide at the expense of the sulphinic acid. In order to obtain the maximum yields of the thioxanthone, it is therefore necessary to employ an excess of sulphinic acid beyond that required by theory, and since even then the yields are not good, the method cannot be recommended for the preparation of the thioxanthones in large quantities.

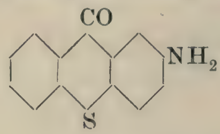
Setting out from a sulphinic acid of known constitution, it is evident that the structure to be assigned to the resulting thioxanthone must be chosen from two alternative formulæ which differ in the position taken by the sulphur with respect to the hydroxy- or amino-groups. The alternatives may be illustrated with the case of the condensation of *p*-toluenesulphinic acid with *m*-hydroxybenzoic acid:



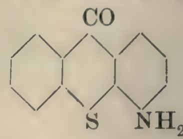
(I.) (II.) (III.)

From the general results obtained in studying the influences which govern the sulphination of hydroxy-derivatives of benzene, the second type of alternative (II) cannot be entertained as highly probable, for it has been shown that the course of this reaction is susceptible to the influence of "steric" conditions; thus, in forming a substance of type II, not only must ortho-condensation occur in preference to the more general para-condensation, but in forming the parental carboxylic acid (III) it must take place under the more adverse steric conditions. For these reasons we consider that preference must be given to the first type of formula (I), which involves the para-condensation, and the contention is supported in the case of the aminothioxanthone furnished by benzenesulphinic acid and *m*-aminobenzoic acid. The substances possessing the alternative structures in question, 2- and 4-aminothioxanthones (IV and V), have been prepared by F. Mayer (*Ber.*, 1909, **42**, 3046) with methods which leave no room for doubt as to the constitution of the products. These substances melt respectively at 222° and

203°, whilst that obtained by ourselves melts at the temperature ascribed to the first-named isomeride. We take this opportunity



(IV).



(V.)

of expressing our thanks to Dr. Mayer for kindly placing at our disposal a small quantity of the 2-amino-derivative. A close comparison of this substance with that obtained by ourselves finally proved the identity of the latter.

Since there is no reason to suspect that the *o*- and *p*-toluenesulphinic acids should behave differently from benzenesulphinic acid, a corresponding structure has been assigned to other amino- and hydroxy-derivatives of thioxanthone which have been prepared from those substances.

It is evident that the method of synthesis now described may be further varied by changing the situation of the carboxyl group in the components; thus an *o*-carboxy-sulphinic acid may be condensed with a simple aromatic compound:

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{SO_2H}{CO_2H}} + C_6H_6 = C_6H_4{<}{\genfrac{}{}{0pt}{}{-S-}{CO}}{>}C_6H_4 + 2H_2O + O.$$

but no experiments dealing with this method are described in the present paper, for a typical case has already been investigated (Davis and Smiles, Trans., 1910, **97**, 1290), when thioxanthone was prepared from *o*-carboxybenzenesulphinic acid and benzene.

The substances described in the experimental part of this paper are by no means the sole products of the various interactions; in fact, it is not easy with the usual methods to isolate the thioxanthones from the impure products, and were it not for the help of a method of fractional sublimation (Christopher, Proc., 1911, **27**, 236) it is doubtful whether these experiments could have been brought to a successful conclusion.

Experimental.

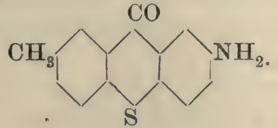
2-Aminothioxanthone, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CO}{S}}{>}C_6H_3{\cdot}NH_2$.

An intimate mixture of 10 grams of *m*-aminobenzoic acid with 23 grams of benzenesulphinic acid was heated at 170—190° for four hours. The cold mass was boiled with aqueous sulphuric acid, and then, after being rendered alkaline with alkali hydroxide, the mixture was repeatedly extracted with ether. The united extracts were shaken with diluted sulphuric acid, and the aqueous layer,

which contained the sparingly soluble sulphate, was treated with alkali to liberate the base. The greenish-yellow precipitate was collected, and when dry it was sublimed in a vacuum. The product formed orange needles, which melted at 222°, whether heated alone or mixed with 2-aminothioxanthone obtained from another source (F. Mayer, *loc. cit.*). (Found, C=68·8; H=3·8. Calc., C=68·7; H=3·9 per cent.)

The substance also possessed the other physical properties elsewhere attributed to 2-aminothioxanthone.

2-*Amino-7-methylthioxanthone*,



The preparation of this substance from *m*-aminobenzoic acid and *p*-toluenesulphinic acid was conducted in the same manner as that described with 2-aminothioxanthone. However, the yields were extremely poor, and unfortunately an accident which occurred during the analysis of the small quantity available rendered invalid the estimation of hydrogen in this substance:

0·1366 gave 0·3506 CO_2. C=70·0.

$C_{14}H_{11}ONS$ requires C=69·71 per cent.

The substance forms orange needles, which melt at 190°, whilst other physical properties are similar to those of the 2-amino-derivative.

2-*Hydroxy-7-methylthioxanthone*,

$$C_6H_3Me{<}{\overset{CO}{\underset{S}{}}}{>}C_3H_3{\cdot}OH.$$

Interaction of 10 grams of *m*-hydroxybenzoic acid with 23 grams of *p*-toluenesulphinic acid was effected by heating the mixture at 190° during four hours. The cold mass was boiled with aqueous sodium hydroxide, and then the phenols were liberated from the solution by saturation with carbonic acid. The semi-solid precipitate was dissolved in ether, and the solution was shaken with excess of aqueous alkali hydroxide. A considerable quantity of material dissolved in the latter medium, forming a deep orange-coloured solution; this was kept for twenty-four hours, when the sparingly soluble sodium salt of the required thioxanthone separated in flocculent masses of needles. The hydroxythioxanthone obtained by treating this sodium salt with dilute mineral acid was almost pure, but it was further purified by sublimation in a vacuum. The

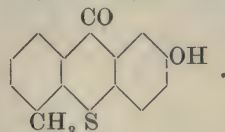
product, 2-hydroxy-7-methylthioxanthone, formed large, lemon-yellow needles, which showed a metallic lustre; these melted at 217°, and dissolved in concentrated sulphuric acid, imparting a brilliant green fluorescence to that medium:

0·1149 gave 0·2910 CO_2 and 0·0426 H_2O. C = 69·0; H = 4·2.

$C_{14}H_{10}O_2S$ requires C = 69·4; H = 4·1 per cent.

The sodium salt of this substance separates in orange needles from an alkaline aqueous solution of the phenol. The latter is sparingly soluble in most cold organic media, but it may be recrystallised from hot acetic acid, in which it is moderately soluble.

2-Hydroxy-5-methylthioxanthone,



The preparation of this hydroxy-derivative was conducted in the manner described in the foregoing paragraph, *m*-hydroxybenzoic and *o*-toluenesulphinic acids being heated together in quantities of 10 and 23 grams respectively. The yields obtained were somewhat poorer than with *p*-toluenesulphinic acid, partly on account of the greater solubility of the sodium salt in the alkaline medium. The product was purified as usual by sublimation in a vacuum, when it was obtained in yellow needles, which melted at 211°:

0·0755 gave 0·1926 CO_2 and 0·029 H_2O. C = 69·5; H = 4·2.

$C_{14}H_{10}O_2S$ requires C = 69·4; H = 4·1 per cent.

Other physical properties of this substance are similar to those of the 7-methyl derivative.

Hydroxythioxanthone, $C_6H_4{<}^{CO}_{S}{>}C_6H_3{\cdot}OH$.

In some previous experiments (Davis and Smiles, *loc. cit.*) a hydroxythioxanthone was obtained by condensation of *o*-thiolbenzoic acid with phenol in the presence of warm concentrated sulphuric acid. Although by heating this substance water could not be expelled from it, the suggestion was offered that it crystallises with water, for repeated fractionation did not appreciably alter the composition. In view of the fact that the methyl derivatives do not crystallise in this manner, it was considered necessary to re-investigate the simpler substance in order to determine the cause of the apparent divergence of properties. It appeared probable that an oxide of the thioxanthone might have been present as an

impurity, for observations from numerous sources have shown that sulphides are apt to be oxidised on prolonged heating with sulphuric acid; but beyond fractional crystallisation, a method of removing substances of this type from the mixture could not be devised until the formation of the methyl derivatives from the sulphinic acids had been investigated. From the alkaline mother liquors whence the sodium salts of these substances had separated, more soluble salts were isolated by adding concentrated alkali hydroxide. The substances obtained from these by mineral acids resisted all attempts at complete purification; but there is little doubt that they are the oxides of the corresponding hydroxythioxanthones which have escaped reduction by the excess of the sulphinic acid. When heated in a vacuum at 200° they char and furnish a sublimate of the thioxanthone. The solubility of the sodium salts of these substances suggested a means of removing similar impurities from the crude hydroxythioxanthone, and the following method of preparation was adopted.

It was found that the yield of hydroxythioxanthone may be much improved by employing a relatively large quantity of phenol, for much of this substance is removed by sulphonation during the course of the interaction with *o*-thiolbenzoic acid. In other respects the condensation was effected as previously described. The product obtained by adding the mixture to water was dissolved in hot 2*N*-alkali hydroxide, and on cooling the solution the sodium salt of hydroxythioxanthone separated in orange needles. These were collected, and washed with the cold medium, in which they are almost insoluble. The purified phenol was liberated from this sodium salt with mineral acid, and it was eventually sublimed in a vacuum at 200°:

0·1067 gave 0·2655 CO_2 and 0·3569 H_2O. $C=67·9$; $H=3·7$.

$C_{13}H_8O_2S$ requires $C=68·4$; $H=3·5$ per cent.

The *hydroxythioxanthone* thus obtained forms large, lemon-yellow needles, which exhibit a metallic lustre, and melt at 243°. The substance is very sparingly soluble in most cold organic media, and its orange-coloured sodium salt is almost insoluble in cold water.

In conclusion we desire to express our thanks to the Research Fund Committee of the Society for a grant which has defrayed the cost of these experiments.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE, LONDON.

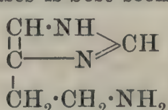
CCXXXII.—*Some Derivatives of 4(or 5)-Methylglyoxaline.*

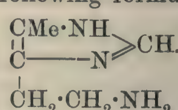
By ARTHUR JAMES EWINS.

THE recent discovery of the high degree of physiological activity attaching to the base 4(or 5)-β-aminoethylglyoxaline (Dale and Laidlaw, *J. Physiol.*, 1910, **41**, 318) and its possible therapeutical importance, has served to stimulate research in the direction of glyoxaline derivatives generally. The most interesting result so far has been the synthesis and resolution of the biochemically important amino-acid histidine (α-amino-β-glyoxaline-4(or 5)-propionic acid) by Pyman (this vol., p. 1386), who has also devised a new synthetic method of preparing the base 4(or 5)-β-aminoethylglyoxaline (this vol., p. 668) in place of the tedious and expensive method employed by Windaus and Vogt (*Ber.*, 1907, **40**, 3691). Of the numerous derivatives obtained in the course of this work, however, none was found to be possessed of physiological activity in any marked degree.

Quite recently Windaus and Opitz (*Ber.*, 1911, **44**, 1721) have obtained the alcohol 4(or 5)-β-hydroxyethylglyoxaline corresponding with the active base already mentioned, and, moreover, have synthesised 4(or 5)-β-aminomethylglyoxaline, the lower homologue of this base. From experiments carried out in these laboratories, this new base has been found, however, to be almost devoid of physiological action.

The present communication deals in the main with the synthesis of a methyl homologue of 4(or 5)-β-aminoethylglyoxaline, namely, 4(or 5)-methyl-5(or 4)-β-aminoethylglyoxaline, which it was expected might prove physiologically interesting. The structural relationship of the two bases is best seen from the following formulæ:


4(or 5)-β-Amino-ethylglyoxaline.


4(or 5)-Methyl-5(or 4)-β-amino-ethylglyoxaline.

these bases in each case being tautomeric (compare Pyman, Trans., 1910, **97**, 1814).

The synthesis of this methyl homologue of 4(or 5)-β-aminoethylglyoxaline was suggested by an observation made by Windaus (*Ber.*, 1909, **42**, 758). It had been recorded by O. Gerngross (*Ber.*, 1909, **42**, 398) that 4(or 5)-methylglyoxaline on treatment with chloral formed an additive product, which he considered to be

4-$\gamma\gamma\gamma$-trichloro-β-hydroxypropylglyoxaline, the reaction being formulated thus:

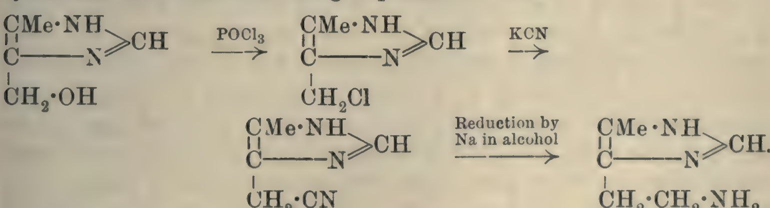
$$CCl_3\cdot CHO + \begin{array}{l} CH_3\cdot C\cdot NH \\ \qquad\quad \| \\ \qquad\quad C\text{---}N \end{array}\!\!\!\!\!\! > CH = \begin{array}{l} CCl_3\cdot CH(OH)\cdot CH_2\cdot C\cdot NH \\ \qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\quad C\text{---}N \end{array}\!\!\!\!\!\! > CH.$$

Windaus (*loc. cit.*), however, found that 4(or 5)-methylglyoxaline on treatment with formaldehyde yielded a product which on reduction gave 4:5-dimethylglyoxaline. The additive product must therefore be produced according to the equation:

$$H\cdot CHO + \begin{array}{l} CMe\cdot NH \\ \| \\ CH\text{----}N \end{array}\!\!\!\!\!\! > CH = \begin{array}{l} \qquad\qquad CMe\cdot NH \\ \qquad\qquad \| \\ HO\cdot CH_2\cdot C\text{-----}N \end{array}\!\!\!\!\!\! > CH.$$

The methylhydroxymethylglyoxaline so produced was not obtained by Windaus in a pure condition; but as the required 4(or 5)-methyl-5(or 4)-aminoethylglyoxaline should be readily obtainable from this hydroxy-derivative by a series of reactions analogous to those employed by Pyman in the conversion of 4(or 5)-hydroxymethylglyoxaline into 4(or 5)-β-aminoethylglyoxaline, the work of Windaus was repeated with a view to the isolation of 4(or 5)-methyl-5(or 4)-hydroxymethylglyoxaline in the pure state. This was readily accomplished after slightly modifying the conditions of Windaus's experiment, and a good yield (50 per cent. of the theory) of the base was isolated by means of its pure, crystalline picrate.

The conversion of 4(or 5)-methyl-5(or 4)-hydroxymethylglyoxaline into the required base was carried out on the lines of Pyman's synthesis, the reactions being represented thus:



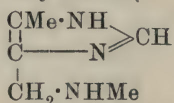
For the conversion of 4(or 5)-hydroxymethylglyoxaline into the corresponding chloro-derivative Pyman employed phosphorus pentachloride. This reagent was found to be unsuitable in the case of the methyl homologue. With the hydrochloride of the chloro-derivative no reaction occurred in the cold (compare Pyman), and with the free base, or on heating with the hydrochloride, a considerable amount of charring occurred. By employing phosphoryl chloride, however, the reaction proceeded quite smoothly, and a quantitative yield of the chloro-derivative was obtained.

Like 4(or 5)-chloromethylglyoxaline, the methyl homologue is extremely reactive; thus on treating a freshly prepared ice-cold

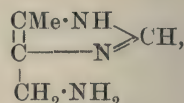
aqueous solution of the base with a similarly cold solution of picric acid, a crystalline picrate was obtained, which was found to consist of nearly pure 4(or 5)-methyl-5(or 4)-hydroxymethylglyoxaline picrate, the chlorine atom of the base having been replaced by hydroxyl by the action of the water even at 0°.

The conversion of 4(or 5)-methyl-5(or 4)-chloromethylglyoxaline into the corresponding cyano-compound and the reduction of the latter to the ethylamine base followed exactly on the lines of Pyman's synthesis.

By the action of cold aqueous methylamine and of cold concentrated aqueous ammonia on 4(or 5)-methyl-5(or 4)-chloromethylglyoxaline, two other bases, namely, 4(or 5)-*methyl*-5(or 4)-*methylaminomethylglyoxaline* (I) and 4(or 5)-*methyl*-5(or 4)-*aminomethylglyoxaline* (II), were obtained, although the yields obtained were comparatively small (10—20 per cent.).



(I.)



(II.)

With the exception of 4(or 5)-methyl-5(or 4)-cyanomethylglyoxaline and of 4(or 5)-methyl-5(or 4)-β-aminoethylglyoxaline, all the glyoxaline derivatives obtained during the course of this investigation give an intense red colour with *p*-diazobenzenesulphonic acid in alkaline solution (Pauly's histidine reagent, *Zeitsch. physiol. Chem.*, 1904, **42**, 508). It may be also mentioned that it appears to be a general property of glyoxaline derivatives that they form phosphotungstates, which are soluble in hot water or cold acetone, and may usually be crystallised from dilute acetone, a property which is often of considerable advantage as a means of separation and purification.

The physiological action of the various bases obtained during the course of this work was investigated by Dr. P. P. Laidlaw, of these laboratories, to whom the author wishes to express his thanks. It was found that the bases 4(or 5)-methyl-5(or 4)-aminomethylglyoxaline and 4(or 5)-methyl-5(or 4)-methylaminomethylglyoxaline were physiologically almost inactive. 4(or 5)-Methyl-5(or 4)-β-aminoethylglyoxaline was, however, found to be physiologically active, chiefly in producing a decided fall in blood pressure (vasodilator effect) when injected intravenously, similar to, although somewhat less powerful than, that produced by 4(or 5)-β-aminoethylglyoxaline. It has also a motor effect on plain muscle, but its activity in this direction is far less (only about 1/200th or less) than that produced by the last-mentioned base.

Experimental.

Interaction of 4(or 5)-*Methylglyoxaline and Formaldehyde.*

Five grams of 4(or 5)-methylglyoxaline were heated in a sealed tube for two hours at 120° with 10 c.c. of a 40 per cent. solution of formaldehyde. There was no pressure on opening the tube, and to the clear, light yellow contents was added a hot saturated aqueous solution of 6·5 grams of picric acid. On cooling, a yellow, crystalline solid separated, which after recrystallisation from dilute (50 per cent.) alcohol was obtained quite pure. Yield, 9 grams.

4(or 5)-*Methyl*-5(or 4)-*hydroxymethylglyoxaline*,

$$\begin{array}{l} CH_3\cdot C\cdot NH \\ \quad\;\; \| \\ HO\cdot CH_2\cdot C\text{—}N \end{array}\!\!>\!CH.$$

The free base was obtained from the picrate by converting the latter into the hydrochloride, and treating the solution so obtained with excess of sodium carbonate. The alkaline solution was evaporated to dryness, the residue extracted with absolute alcohol, and the solution concentrated. On keeping, the crystalline base slowly separated in stout, hexagonal prisms, melting at 138°:

0·1568 gave 0·3074 CO_2 and 0·1002 H_2O. C = 53·5; H = 7·1.
0·3084 „ 68·2 c.c. N_2 (moist) at 23° and 758 mm. N = 25·2.
$C_5H_8ON_2$ requires C = 53·6; H = 7·1; N = 25·0 per cent.

The base is very readily soluble in water or alcohol, but sparingly so in most other organic solvents. Solutions of the base or of its salts give an intense cherry-red coloration with *p*-diazobenzenesulphonic acid. In neutral or alkaline solution it gives a precipitate with mercuric chloride, which is soluble in dilute acid. With phosphotungstic acid solution it gives a precipitate, which is readily soluble in hot water or cold acetone, and may readily be crystallised from dilute acetone, forming fan-shaped clusters of short, broad prisms.

The *hydrochloride*, obtained from the picrate in the usual manner, crystallises from absolute alcohol, the yield being increased by addition of a little dry ether. It forms stout, hexagonal plates, melting at 240—242°. The salt is deliquescent, and readily soluble in water or alcohol:

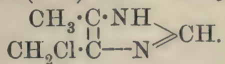
0·1658 gave 0·2440 CO_2 and 0·0892 H_2O. C = 40·1; H = 5·9.
0·1340 „ 22·4 c.c. N_2 (moist) at 23° and 758 mm. N = 19·0.
0 1580 „ 0·1524 AgCl. Cl = 23·8.
$C_5H_8ON_2,HCl$ requires C = 40·3; H = 6·0; N = 18·8; Cl = 24·0 per cent.

The *picrate* obtained as described above crystallises from hot 50 per cent. alcohol in long, thin prisms, melting to a red liquid at 180—181°:

0·1374 gave 0·1938 CO_2 and 0·0410 H_2O. C = 38·5; H = 3·3.
0·2596 „ 47·2 c.c. N_2 (moist) at 25° and 766 mm. N = 20·8.
$C_5H_8ON_2,C_6H_3O_7N_3$ requires C = 38·7; H = 3·2; N = 20·6 per cent.

This salt is very sparingly soluble in cold water or alcohol, but fairly readily so in these solvents when hot.

4(or 5)-*Methyl*-5(or 4)-*chloromethylglyoxaline*,

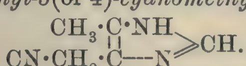


The *hydrochloride* of this base was readily obtained as follows: Five grams of 4(or 5)-methyl-5(or 4)-hydroxymethylglyoxaline hydrochloride were suspended in about 20 c.c. of phosphoryl chloride, and the mixture gently warmed on a sand-bath under a reflux condenser. Hydrogen chloride was evolved, and solution was complete in about fifteen minutes. The excess of phosphoryl chloride was removed by distillation in a vacuum, and the residual syrupy liquid dissolved in a small quantity of hot saturated alcoholic solution of hydrogen chloride. On cooling, the crystalline hydrochloride of 4(or 5) - methyl - 5(or 4) - chloromethylglyoxaline rapidly separated. Precipitation was completed by the addition of a little dry ether. For analysis the salt was recrystallised from absolute alcohol. It forms thin, rectangular plates, melting at 222°. The yield is quantitative:

0·0776 gave 0·1014 CO_2 and 0·0328 H_2O. C = 35·6; H = 4·7.
0·0996 „ 0·1718 AgCl. Cl = 42·7.
$C_5H_7N_2Cl,HCl$ requires C = 35·9; H = 4·8; Cl = 42·5 per cent.

This salt is very readily soluble in cold methyl alcohol.

4(or 5)-*Methyl*-5(or 4)-*cyanomethylglyoxaline*,



This substance was prepared from the corresponding chloro-derivative by the method which was found by Pyman (*loc. cit.*) to yield the best results with 4(or 5)-chloromethylglyoxaline. Fifteen grams of 4(or 5)-methyl-5(or 4)-chloromethylglyoxaline hydrochloride were dissolved in 180 c.c. of absolute alcohol, and the solution slowly added drop by drop to a solution of 50 grams of potassium cyanide in about 60 c.c. of water. The mixture was kept well stirred and at a temperature of 0°. The precipitated salts were collected, washed with alcohol, and the filtrate and washings treated with

90 c.c. of saturated sodium carbonate solution. The mixture was evaporated to dryness under diminished pressure, the residue extracted with warm ethyl acetate, and the solvent evaporated. From the residual brown, syrupy liquid the 4(or 5)-methyl-5(or 4)-cyanomethylglyoxaline crystallised out on keeping. Yield, 2·7 grams (24 per cent. of the theoretical).

For analysis the base was recrystallised from water, when it was obtained in large, rectangular prisms, melting at 163—164°:

0·2274 gave 0·4954 CO_2 and 0·1264 H_2O. C = 59·4; H = 5·7.

0·1194 „ 34·0 c.c. N_2 (moist) at 15° and 772 mm. N = 34·7.

$C_6H_7N_3$ requires C = 59·5; H = 5·8; N = 34·7 per cent.

4(or 5)-*Methyl*-5(or 4)-*cyanomethylglyoxaline* is moderately soluble in cold, and very readily so in hot, water. Solutions of the base give with mercuric chloride a white precipitate, soluble in dilute acids. The *phosphotungstate* of the base is almost insoluble in cold water, but readily soluble in hot water or cold acetone. It crystallises from dilute acetone in long needles. With *p*-diazobenzenesulphonic acid in alkaline solution (sodium carbonate) an intense deep reddish-brown coloration is produced, the colour being strikingly different from that usually given by simple glyoxaline derivatives.

The *picrate* crystallises from hot water in prisms melting at 172°.

4(or 5)-*Methyl*-5(or 4)-*β-aminoethylglyoxaline*,

$$\left.\begin{array}{r} CH_3\cdot C{:}NH \\ \| \quad\; \\ NH_2\cdot CH_2\cdot CH_2\cdot C{-\!-}N \end{array}\right\rangle CH.$$

The reduction of 4(or 5)-methyl-5(or 4)-cyanomethylglyoxaline to the required base was carried out by means of sodium in concentrated alcoholic solution.

2·5 Grams of 4(or 5)-methyl-5(or 4)-cyanomethylglyoxaline were dissolved in a minimum quantity of absolute alcohol, and 6·5 grams of sodium was added in small portions to the gently boiling solution. Alcohol was added from time to time as necessary. The solution was then made acid to Congo-red by addition of concentrated hydrochloric acid, and the precipitated salt collected. The filtrate was rendered alkaline with sodium carbonate, evaporated to dryness, and dissolved in a little absolute alcohol. On keeping, nothing separated out, and the solution was then treated with a hot saturated solution of picric acid. The crystalline *picrate* of 4(or 5)-methyl-5(or 4)-β-aminoethylglyoxaline rapidly separated. Yield, 2·7 grams (22 per cent. of the theoretical):

0·1594 gave 0·2158 CO_2 and 0·0402 H_2O. C = 36·9; H = 2·8.

0·1100 „ 20·2 c.c. N_2 (moist) at 19° and 761 mm. N = 21·2.

$C_6H_{11}N_3,(C_6H_3O_7N_3)_2$ requires C = 37·0; H = 2·9; N = 21·6 per cent.

The *dihydrochloride* crystallises from absolute alcohol in colourless, prismatic needles, melting at 231—232°:

0·1295 gave 0·1732 CO_2 and 0·0801 H_2O. C = 36·5; H = 6·8.

$C_6H_{11}N_3,2HCl$ requires C = 36·7; H = 6·6 per cent.

This salt is anhydrous, very sparingly soluble in hot absolute alcohol, very readily so in cold water, and fairly readily so in cold methyl alcohol. With *p*-diazobenzenesulphonic acid in alkaline solution a reddish-yellow colour is produced. The aqueous solution of the salt is precipitated by mercuric chloride, the precipitate being soluble in dilute acids. The phosphotungstate of the base is readily soluble in hot water or in cold acetone.

The *dihydrobromide* crystallises from absolute alcohol, on addition of dry ether, in stout, hexagonal prisms, melting at 212°:

0·1028 gave 0·1348 AgBr. Br = 55·8.

$C_6H_{11}N_3,2HBr$ requires Br = 55·8 per cent.

4(or 5)-*Methyl*-5(or 4)-*methylaminomethylglyoxaline*,

$$\begin{array}{r}CH_3\cdot C\cdot NH\\ \| \quad\\ CH_3\cdot NH\cdot CH_2\cdot C{-}N\end{array}\!\!>\!CH.$$

This base was obtained by the action of methylamine on 4(or 5)-methyl-5(or 4)-chloromethylglyoxaline.

0·5 Gram of 4(or 5)-methyl-5(or 4)-chloromethylglyoxaline was dissolved in a few c.c. of methyl alcohol, and the solution added drop by drop to 2·5 c.c. of an aqueous solution of methylamine, which was kept at a temperature of about 0°. The solution was then evaporated to dryness, the residue dissolved in a little water, and treated with a hot saturated aqueous solution of picric acid. The heavy, yellow oil which separated from the hot solution was collected, and from the filtrate on cooling the crystalline 4(or 5)-*methyl*-5(or 4)-*methylaminomethylglyoxaline dipicrate* separated. It crystallises from water in prisms melting at 222°. Yield, 20 per cent. of theory:

0·1218 gave 0·1654 CO_2 and 0·0352 H_2O. C = 37·0; H = 3·2.

0·0944 ,, 17·4 c.c. N_2 (moist) at 16° and 764 mm. N = 21·6.

$C_6H_{11}N_3,(C_6H_3O_7N_3)_2$ requires C = 37·0; H = 2·9; N = 21·6 per cent.

The *dihydrochloride* crystallises from absolute alcohol in stout prisms, melting at 246—247°:

0·1014 gave 0·1480 AgCl. Cl = 36·1.

$C_6H_{11}N_3,2HCl$ requires Cl = 36·2 per cent.

4(or 5)-*Methyl*-5(or 4)-*aminomethylglyoxaline*,

$$\begin{array}{l} \quad\quad\quad CH_3\cdot C\cdot NH \\ \quad\quad\quad\quad\ \| \quad\quad\quad \gg CH. \\ NH_2\cdot CH_2\cdot C\text{---}N \end{array}$$

This base was obtained from 4(or 5)-methyl-5(or 4)-chloromethylglyoxaline by the method employed for the preparation of the foregoing base, using concentrated aqueous ammonia (0·88) in place of methylamine. The yield of base was very poor, amounting to only 10 per cent. of the theory.

The *picrate* crystallises from hot water in clusters of well-formed prisms, melting at 216—217°:

0·0934 gave 0·1224 CO_2 and 0·0240 H_2O. C=35·7; H=2·8.

$C_5H_9N_3,(C_6H_3O_7N_3)_2$ requires C=35·8; H=2·6.

The *hydrochloride* crystallises from absolute alcohol in stout, rectangular prisms, melting at 233—234°.

Solutions both of this and of the foregoing base give with *p*-diazobenzenesulphonic acid an intense cherry-red colour.

The greater part of the analytical work in connexion with this investigation has been carried out by Mr. C. J. Gobell, to whom the author wishes to express his thanks.

THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
HERNE HILL, LONDON, S.E.

CCXXIII.—*The Triazo-group. Part XIX. Nitrosoazides of Dipentene,* d-*Limonene, and* l-*Limonene.*

By MARTIN ONSLOW FORSTER and FREDERIK MARINUS VAN GELDEREN.

IT has been shown that the nitrosate of trimethylethylene readily exchanges the $O\cdot NO_2$-group for the azoimide nucleus (this vol., p. 239), yielding the oxime of the triazoketone,

$$(CH_3)_2CN_3\cdot CO\cdot CH_3,$$

and that the nitrosochlorides of pinene and terpineol undergo a similar transformation into the corresponding nitrosoazides (*loc. cit.*, p. 244). α-Triazocamphoroxime (Trans., 1907, **91**, 874), although obtained by a different process, may be looked upon as the earliest representative of this class, and with the object of gaining further information as to the applicability of the reaction above indicated,

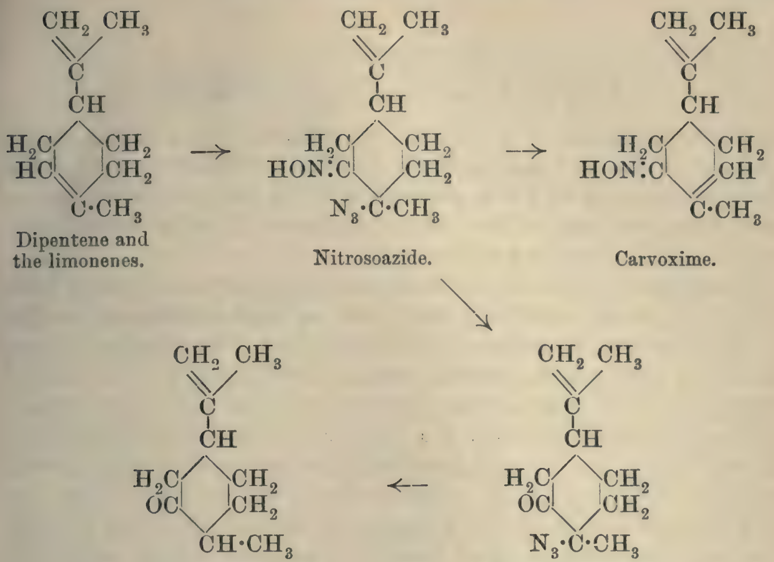
and the behaviour of the triazo-group in the products, we have prepared nitrosoazides of dipentene, *d*-limonene, and *l*-limonene.

The first point brought to light is the facility with which dipentene nitrosate yields the nitrosoazide, the proportion of which is greatly in excess of that derived from trimethylethylene nitrosate, and in this respect it resembles pinene nitrosochloride. Dipentene nitrosochloride also lends itself with great readiness to interaction, but the limonene nitrosoazides are associated with such a large proportion of oily by-products that the yield sinks to the neighbourhood of 20 per cent. A similar difficulty was encountered by Leach (Trans., 1905, **87**, 413) in connexion with the limonene nitrosocyanides, which were accompanied by 60 per cent. of oil, even in the most favourable circumstances.

The well-known experiments of Wallach (*Annalen*, 1889, **252**, 113, and 1892, **270**, 181) dealing with the preparation of nitrolamines from the limonene nitrosochlorides, coupled with the fact that Leach isolated the α- and β-nitrosocyanides, led to the expectation that the isomeric nitrosoazides would be obtainable from each hydrocarbon; in this we were disappointed, however, only one derivative being isolated alike from the α- and the β-nitrosochlorides. As Leach's experiments showed that the yield of β-nitrosocyanide amounted to only 2 or 3 per cent., it is probable that the missing nitrosoazide is concealed in the large proportion of oil with which the crystalline product is associated.

The correspondence in structure between the new nitrosoazides and the nitrosocyanides follows from their chemical behaviour. The presence of the *iso*nitroso-group is demonstrated by interaction with phenylcarbimide, although benzoyl and acetyl derivatives could not be isolated in solid form. Removal of the elements of hydrazoic acid leads to the respective carvoxime, whilst application of Wallach's process of hydrolysis (*Annalen*, 1906, **346**, 231) eliminates the oximino-group, and gives rise to the corresponding triazodihydrocarvone.

As appears from the formula on p. 2061, triazodihydrocarvone belongs to the class of triazoketones in which the triazotised carbon atom is tertiary, and in accordance with the principles already developed, distinguishes itself from triazocamphor and triazoacetone in its behaviour towards alcoholic alkali hydroxide, which does not set free two-thirds the azidic nitrogen, but eliminates the triazo-group in the form of alkali azide. It has been prepared in three forms, inactive from dipentene, and having strong dextro- and lævo-rotatory power when produced from *d*- and *l*-limonenes respectively. Their oximes are, of course, the nitrosoazides from which the ketones are directly obtainable by hydrolysis; the triazoketones



Dipentene and the limonenes. Nitrosoazide. Carvoxime. Dihydrocarvone. Triazodihydrocarvone.

yield also well-crystallised semicarbazones, but we have not been able to prepare thiosemicarbazones, semioxamazones, or phenylhydrazones. The following table summarises the physical properties of the compounds under discussion:

	Inactive.	Dextrorotatory.	Lævorotatory.
Triazodihydrocarvone	b. p. 81°/0·4 mm.	b. p. 93°/0·46 mm.	b. p. 93—94°/0·48 mm.
Oxime	m. p. 72—73°	m. p. 52—53°	m. p. 52—53°
Phenylcarbamyloxime	m. p. 113—114°	m. p. 114—115°	m. p. 114—115°
Semicarbazone	m. p. 132—133°	m. p. 220°	m. p. 220°

It was to be expected that the reduction of triazodihydrocarvone would lead to the unknown aminoketone, or at least to the dihydropyrazine derivative corresponding with it, this alternative having been rendered probable by our experiments with the ketone from trimethylethylene nitrosoazide (this vol., p. 243). The action, however, takes a different course. Elemental nitrogen is eliminated, but the resulting aminoketone immediately loses its amino-group, which is exchanged for hydrogen, dihydrocarvone being the product. This unexpected result recalls the experience of Wallach (*Annalen*, 1898, **300**, 290, and 1900, **313**, 368), who encountered the same ketone among the products of reduction of the dibromide of nitrosopinene.

Experimental.

Dipentene Nitrosoazide, $C_{10}H_{15}(:NOH)\cdot N_3$.

The hydrocarbon used for these experiments boiled at 174—176°, had D^{18} 0·8653, and gave α_D 2°42′ in a 2-dcm. tube, whence $[\alpha]_D$ 1·5°. It was converted into the nitrosate and the nitrosochloride by the recognised methods, either of these materials being suitable for transformation into the nitrosoazide.

Twenty-five grams of the additive compound were covered with 50 c.c. of alcohol and a concentrated aqueous solution of sodium azide containing 15 grams; during seven days the suspended matter gradually passed into solution, crystals of sodium chloride or nitrate appearing. On pouring the mixture into cold water, the turbid product deposited crystals, the yield of nitrosoazide representing more than 80 per cent. of the theoretical amount; as the nitrosochloride of dipentene is a more economical product than the nitrosate, and there does not appear to be any difference between the two substances in their behaviour towards sodium azide, the nitrosochloride was always employed in the later experiments:

0·2513 gave 57·1 c.c. N_2 at 17° and 777 mm. N = 27·34.

$C_{10}H_{16}ON_4$ requires N = 26·92 per cent.

The substance is readily soluble in organic solvents, and is best crystallised from methyl alcohol, which deposits lustrous, rhombic plates, melting at 72—73°. It effervesces vigorously with concentrated sulphuric acid, and somewhat slowly with stannous chloride in hydrochloric acid, liberation of gas becoming more marked on warming. The nitrosoazide is volatile in steam, and is not dissolved by aqueous alkalis, which fail to remove either the oximino- or the triazo-group; with alcoholic alkali hydroxide, however, the elements of hydrazoic acid are eliminated, the product being inactive carvoxime, m. p. 93°.

The *phenylcarbamyl* derivative, $C_{10}H_{15}(:NO\cdot CO\cdot NH\cdot C_6H_5)\cdot N_3$, prepared by mixing molecular proportions of dipentene nitrosoazide and phenylcarbimide in dry benzene, crystallised in needles on adding petroleum, and after recrystallisation from boiling petroleum melted at 113—114°:

0·1006 gave 18·7 c.c. N_2 at 23° and 769 mm. N = 21·69.

$C_{17}H_{21}O_2N_5$ requires N = 21·40 per cent.

The substance is insoluble in cold petroleum, but dissolves readily in the hot liquid and in cold alcohol, ether, or benzene.

i-*Triazodihydrocarvone*, $\begin{matrix}CH_2\\CH_3\end{matrix}\!\!>\!C\cdot CH\!<\!\begin{matrix}CH_2—CO\\CH_2\cdot CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}CH_3\\N_3\end{matrix}$.

Attempts to hydrolyse dipentene nitrosoazide with mineral acids having shown that carvacrol is produced, the triazoketone was prepared by the action of hot aqueous oxalic acid. In quantities of 5 grams the oxime was mixed with oxalic acid (15 grams) in concentrated solution, when a current of steam carried over about 50 per cent. of a colourless oil, which was extracted with ether, dried with sodium sulphate, and distilled with the Gaede pump:

0·1740 gave 32·8 c.c. N_2 at 18° and 756 mm. N = 22·00.

$C_{10}H_{15}ON_3$ requires N = 21·76 per cent.

The triazoketone has a pleasant odour of peppermint, and rapidly becomes yellow, even when protected from light; it boils at 81°/0·4 mm., and has D^{20} 1·0409. Although effervescence with concentrated sulphuric acid is very vigorous, action with stannous chloride is sluggish, even on warming, and alkalis do not liberate nitrogen. When heated in alcohol with hydroxylamine acetate the triazoketone regenerates the nitrosoazide.

The *semicarbazone*, $C_{10}H_{15}(:N\cdot NH\cdot CO\cdot NH_2)\cdot N_3$, prepared from *i*-triazodihydrocarvone and semicarbazide acetate in dilute alcohol, separates rapidly, and after crystallisation from benzene diluted with petroleum melts at 132—133°:

0·1450 gave 42·9 c.c. N_2 at 16° and 747 mm. N = 34·30.

$C_{11}H_{18}ON_6$ requires N = 33·60 per cent.

The substance is freely soluble in ordinary solvents, excepting petroleum.

Reduction with Aluminium Amalgam.—In the hope of obtaining the aminoketone, *i*-triazodihydrocarvone was reduced in moist ether with aluminium amalgam. Nitrogen was liberated, and about 70 per cent. of non-basic material was produced; this yielded an oxime, which after recrystallisation from alcohol melted at 112—113°:

0·1147 gave 0·3020 CO_2 and 0·1069 H_2O. C = 71·81; H = 10·43.
0·1649 ,, 12·15 c.c. N_2 at 16° and 766 mm. N = 8·77.

$C_{10}H_{17}ON$ requires C = 71·86; H = 10·18; N = 8·38 per cent.

On searching for substances having this composition, it was found that the properties of the oxime correspond with those of dihydrocarvoxime (Wallach, *Annalen*, 1898, **300**, 290, and 1900, **313**, 368). Hence the principal effect of reduction is to replace the triazo-group by hydrogen, a result which is quite unusual, and the aminoketone could not be recognised. A very small quantity of a basic substance was produced, however, melting at 125°, and forming a platini-

chloride decomposing at 217°; owing to insufficiency of material it could not be investigated further, but is probably the dihydropyrazine derivative corresponding with that obtained from aminocamphor and from β-triazo-β-methylbutan-γ-one (this vol., p. 239).

d-*Limonene Nitrosoazide*, $C_{10}H_{15}(:NOH)\cdot N_3$.

The specimen of *d*-limonene employed had D^{18} 0·8474, and gave α_D 102°15′ in a 1-dcm. tube, whence $[\alpha]_D$ 120·6°. It was converted into the nitrosochlorides, which were then separated in order to ascertain whether the β-nitrosochloride gave a triazo-compound distinct from that into which the α-nitrosochloride is converted. No difference being recognised, the mixture of nitrosochlorides was used in subsequent experiments; the conditions of transformation into the nitrosoazide were the same as those observed in the preparation of dipentene nitrosoazide, excepting that the product was extracted with ether instead of being allowed to crystallise from the diluted alcoholic solution. The yield, however, was greatly inferior to that obtained from the inactive hydrocarbon, for the crystals deposited on evaporating the ether amounted to between 20 and 40 per cent. of the theoretical quantity, the remainder persisting as an oil. After recrystallisation from diluted methyl alcohol, the substance melted at 52—53°:

0·2283 gave 51·3 c.c. N_2 at 16° and 780 mm. N = 27·27.

$C_{10}H_{16}ON_4$ requires N = 26·92 per cent.

A solution containing 0·2970 gram, made up to 25 c.c. with chloroform, gave α_D 0°14′ in a 3-dcm. tube, whence $[\alpha]_D$ 6·5°. It dissolves readily in the ordinary organic solvents, but is difficult to crystallise. The behaviour towards sulphuric acid and towards stannous chloride is the same as that of the inactive azide, and alcoholic alkali hydroxide gives rise to *l*-carvoxime, melting at 71—72°, and having $[\alpha]_D$ −33°.

The *phenylcarbamyl* derivative, $C_{10}H_{15}(:NO\cdot CO\cdot NH\cdot C_6H_5)\cdot N_3$.—Although attempts to benzoylate or acetylate the nitrosoazide did not lead to a solid product, phenylcarbimide was found to act readily on the substance in dry benzene, which was subsequently evaporated under reduced pressure until crystallisation began, when the residue was dissolved in methyl alcohol; this yielded crystals on slow evaporation following slight dilution, but the substance was much more difficult to isolate than the inactive isomeride. Recrystallisation from hot petroleum gave lustrous, transparent prisms, melting at 114—115°:

0·1508 gave 28·3 c.c. N_2 at 23° and 763 mm. N = 21·73.

$C_{17}H_{21}O_2N_5$ requires N = 21·40 per cent.

A solution containing 0·2769 gram, made up to 25 c.c. with chloroform, gave α_D 3°57′ in a 3-dcm. tube, whence $[\alpha]_D$ 118·8°. The substance is freely soluble in cold solvents, excepting petroleum, from which, on slow evaporation, it crystallises in inch-long prisms; it effervesces vigorously with concentrated sulphuric acid, and more moderately with stannous chloride in hydrochloric acid.

d-*Triazodihydrocarvone*, $C_{10}H_{15}ON_3$.

The ketone was prepared by hydrolysing *d*-limonene nitrosoazide with hot aqueous oxalic acid, being carried over in steam, and isolated in the usual manner:

0·1908 gave 35·4 c.c. N_2 at 16° and 762 mm. N = 21·98.

$C_{10}H_{15}ON_3$ requires N = 21·76 per cent.

The substance boils at 93°/0·46 mm., has D^{20} 1·0487, and gave α_D 92°48′ in a 1-dcm. tube, whence $[\alpha]_D$ 88·49°; a solution containing 0·8234 gram, diluted to 20 c.c. with chloroform, gave α_D 11°40′ in a 3-dcm. tube, whence $[\alpha]_D$ 94·4°. In chemical behaviour the ketone resembles the inactive one obtained from dipentene, and when it is heated with hydroxylamine acetate in aqueous alcohol the oxime (*d*-limonene nitrosoazide) is regenerated, m. p. 52—53°.

The *semicarbazone*, $C_{10}H_{15}(:N \cdot NH \cdot CO \cdot NH_2) \cdot N_3$, prepared in the usual manner, showed a tendency to remain viscid; on warming with water, however, the oily impurities were removed, the white solid being then dissolved in glacial acetic acid, and precipitated with water. This treatment was repeated until the melting point was constant at 220°, decomposition occurring at this temperature:

0·2864 gave 83·0 c.c. N_2 at 19° and 761 mm. N = 33·92.

$C_{11}H_{18}ON_6$ requires N = 33·60 per cent.

The substance is freely soluble in ordinary solvents, excepting cold petroleum.

Reduction with Aluminium Amalgam.—As in the case of the inactive triazoketone, the principal product of reduction with aluminium amalgam in moist ether was a ketone free from nitrogen; on converting this into its oxime, the latter was found to melt at 88—89°, and appears to be identical with the active dihydrocarvoxime described by Wallach (*Annalen*, 1893, **275**, 117). Associated with the liquid product was a very small proportion of a crystalline substance melting at 110—112°, and yielding a crystalline platinichloride.

l-*Limonene Nitrosoazide*, $C_{10}H_{15}(:NOH)\cdot N_3$.

The hydrocarbon used for the preparation of the nitrosochlorides had D^{18} 0·8465, and gave α_D $-96°21'$ in a 1-dcm. tube, whence $[\alpha]_D$ $-113·8°$. Proceeding as in the case of the dextrorotatory compound, the yield was again found to be very poor, a large proportion of oily by-products accompanying the solid nitrosoazide, which was recrystallised from diluted methyl alcohol, and melted at 52—53°:

0·0964 gave 23·5 c.c. N_2 at 23° and 758 mm. N = 27·56.

$C_{10}H_{16}ON_4$ requires N = 26·92 per cent.

We have not been able to produce a specimen of this substance with optical activity corresponding with that of the dextrorotatory isomeride; a solution containing 0·3038 gram, made up to 25 c.c. with chloroform, gave only $-2'$ in the 3-dcm. tube, whence $[\alpha]_D$ less than $-1°$.

The *phenylcarbamyl* derivative, $C_{10}H_{15}(:NO\cdot CO\cdot NH\cdot C_6H_5)\cdot N_3$, prepared from *l*-limonene nitrosoazide and phenylcarbimide in benzene, remained as a syrup on evaporating the solvent under reduced pressure, but treatment as before with diluted methyl alcohol followed by hot petroleum gave lustrous, woolly needles, melting at 114—115°:

0·0813 gave 15·3 c.c. N_2 at 23° and 765 mm. N = 21·84.

$C_{17}H_{21}O_2N_5$ requires N = 21·40 per cent.

A solution containing 0·2967 gram, made up to 25 c.c. with chloroform, gave α_D $-4°18'$ in a 3-dcm. tube, whence $[\alpha]_D$ $-120·8°$. The behaviour towards solvents, stannous chloride, and concentrated sulphuric acid is the same as that of the dextrorotatory modification.

l-*Triazodihydrocarvone*, $C_{10}H_{15}ON_3$.

Preparation of this triazoketone was effected by the oxalic acid method, about 60 per cent. of the amount expected being obtained:

0·1523 gave 28·6 c.c. N_2 at 18° and 761 mm. N = 22·05.

$C_{10}H_{15}ON_3$ requires N = 21·76 per cent.

The substance boils at 93—94°/0·48 mm., has D^{20} 1·0472, and gave α_D $-96°50'$ in a 1-dcm. tube at the same temperature, whence $[\alpha]_D$ $-92·47°$; a solution containing 0·8278 gram, diluted to 20 c.c. with chloroform, gave α_D $-11°42'$ in a 3-dcm. tube, whence $[\alpha]_D$ $-94·22°$. No chemical differences between this and the foregoing triazoketones were noticed, and hydroxylamine acetate regenerated *l*-limonene nitrosoazide, m. p. 52—53°.

The *semicarbazone*, $C_{10}H_{15}(:N\cdot NH\cdot CO\cdot NH_2)\cdot N_3$, resembled that

of the dextrorotatory triazoketone in its tendency to remain viscid, but was purified by similar treatment, and melted and decomposed at 220°:

0·1432 gave 41·0 c.c. N_2 at 18° and 762 mm. N = 33·67.

$C_{11}H_{18}ON_6$ requires N = 33·60 per cent.

The substance is freely soluble in the ordinary solvents, excepting cold petroleum.

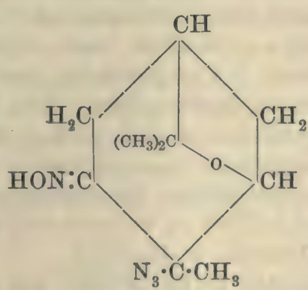
Reduction with Aluminium Amalgam.—Treating *l*-triazodihydrocarvone with aluminium amalgam in moist ether led to a result similar to that recorded for the dextrorotatory and inactive triazo-compounds. The principal product was a non-nitrogenous ketone, identified by means of its oxime with *l*-dihydrocarvone (Wallach and Schrader, *Annalen*, 1894, **279**, 381), along with a minute quantity of a basic solid.

Conversion of the Active Compounds into Derivatives of Dipentene.

Equal amounts of *d*- and *l*-limonene nitrosoazides (m. p. 52—53°) were mixed in methyl alcohol, heated on the water-bath during a short period, and allowed to cool, when the characteristic crystals of dipentene nitrosoazide separated in the course of a few hours; the substance melted at 72—73°, and did not depress the melting point of the nitrosoazide prepared from dipentene.

The *d*- and *l*-triazodihydrocarvones were mixed in ethyl alcohol, and transformed into the semicarbazone, which melted at 132—133° after crystallisation from a mixture of benzene and petroleum; it was identical with the semicarbazone prepared from *i*-triazodihydrocarvone.

Pinol Nitrosoazide,



Pinol, prepared by the action of sodium ethoxide on terpineol dibromide, was converted into the nitrosochloride, this being suspended in dilute alcohol containing sodium azide in the proportion of 4 to 9, and allowed to remain at 40° during half an hour, when the liquid had become clear; very soon afterwards lustrous crystals separated, and after recrystallisation from hot alcohol melted at 160°:

0·1866 gave 0·3704 CO_2 and 0·1231 H_2O. C=54·13; H=7·38.
0·1314 „ 28·3 c.c. N_2 at 20° and 767 mm. N=25·34.
$C_{10}H_{16}O_2N_4$ requires C=53·57; H=7·14; N=25·00 per cent.

The substance is remarkably stable for a member of this class, undergoing no change when heated with aqueous oxalic acid, from which it slowly passes over in the steam; moreover, when heated under reflux during three to four hours with dilute sulphuric acid and a few c.c. of alcohol, the greater part was recovered unchanged, and the liquid exerted only feeble reducing action on Fehling's solution. It dissolves in concentrated hydrochloric acid when gently heated, being precipitated on dilution, and, in consequence, we failed to isolate the corresponding triazoketone.

In conclusion, we wish to express our indebtedness to Sir William Tilden and to Messrs. Schimmel and Co. for valuable specimens with which they were so kind as to furnish us.

Royal College of Science, London.
South Kensington, S.W.

CCXXXIV.—*Preparation of the Betaine of Tryptophan and its Identity with the Alkaloid Hypaphorine.*

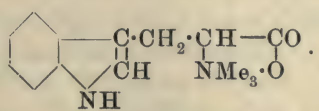
By Pieter van Romburgh and George Barger.

While working in the Botanic Gardens at Buitenzorg, in Java, the late Dr. M. Greshoff (*Mededeelingen uit 's Lands Plantentuin*, 1890, **7**, 29) discovered a crystalline base in the seeds of *Erythrina Hypaphorus*, Boerl., a tree grown for the sake of its shade in the coffee plantations of Eastern Java. The base occurs in the seeds to the extent of about 3 per cent., and to this "alkaloid," for which the name "hypaphorine" was suggested, the formula $C_{14}H_{18}O_2N_2$ was assigned in the "Index Phytochemicus," a list of plant substances published in 1905 by Ritsema and Sack, under the auspices of the Colonial Museum at Haarlem.

In 1891, while still at Buitenzorg, one of us (P. v. R.), at Dr. Greshoff's request, had already joined him in the investigation of the constitution of the new base, and deduced the formula $C_{14}H_{18}O_2N_2$ for it, and had further, after Dr. Greshoff's return to Holland in 1892, shown that on heating with aqueous potassium hydroxide it yielded trimethylamine and indole. The work, subsequently interrupted for many years, was resumed after Dr. Greshoff's death. The results already referred to suggested that

hypaphorine might be a betaine derived from tryptophan, and on methylating a small quantity of this amino-acid, a base was indeed obtained which showed great similarity to hypaphorine (van Romburgh, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 1177). Starting from the same view as to the probable constitution of hypaphorine, the other of us working with larger quantities of tryptophan, independently prepared the same trimethyl derivative.

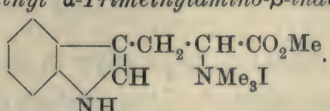
We have now obtained complete proof of the identity of hypaphorine with the betaine formed by methylating tryptophan, so that the alkaloid is α-trimethyl-β-indolepropiobetaine of the following constitution:



Hypaphorine is therefore a base of considerable biochemical interest. It is the first naturally occurring simple derivative of tryptophan. The absence of any pronounced physiological action and its great solubility in water differentiate it from the typical alkaloids (some of which, like strychnine and brucine, are possibly derived from tryptophan by complicated reactions). On the other hand, hypaphorine is a new member of the group of naturally occurring betaines, to which more attention has lately been directed, chiefly owing to the work of E. Schulze and his pupils. In addition to betaine itself, and to hypaphorine, this group at present contains stachydrine, trigonelline, and possibly also trimethylhistidine. The circumstance that hypaphorine is present in the seed to the extent of 3 per cent., and is readily isolated as the nitrate, might perhaps be utilised in a study of the metabolic importance of betaines in the plant, particularly in order to test the view expressed by Winterstein and Trier ("Die Alkaloide," 1910, p. 296) that betaines are merely waste products rendered innocuous by methylation. This question is the more interesting since Staněk (*Zeitsch. physiol. Chem.*, 1911, **72**, 402) has recently arrived at the conclusion that betaine itself is utilised as plastic material in the young shoots and leaves of various plants.

Experimental.

Iodide of Methyl α-Trimethylamino-β-indolepropionate,



This ester is the first reaction product which could be isolated when tryptophan was treated with methyl iodide and sodium

hydroxide according to Engeland's method (*Ber.*, 1910, **43**, 2662). One gram of tryptophan was dissolved in 25 c.c. of methyl alcohol and enough sodium hydroxide to render the solution slightly alkaline. After the addition of 25 c.c. of methyl iodide, the solution was gently boiled for eight hours under a reflux condenser; occasionally a little sodium hydroxide in methyl alcohol was added, in order to keep the reaction alkaline. Finally, the solution was evaporated; the residual syrup at once crystallised on adding cold water; 0·8 gram of crystals was thus obtained, which on recrystallisation from about 25 c.c. of boiling water yielded glistening plates, melting at 197°:

0·1702 gave 0·2928 CO_2 and 0·0805 H_2O. C=46·9; H=5·25.
0·2040 „ 13·2 c.c. N_2 (moist) at 16° and 756 mm. N=7·50.
0·2059 „ 13 c.c. N_2 „ „ 16° „ 757 mm. N=7·33.
0·1650 „ 0·0998 AgI. I=32·7.

$C_{15}H_{21}O_2N_2I$ requires C=46·4; H=5·4; N=7·2; I=32·7 per cent.

Unlike hypaphorine, the above base does not yield a sparingly soluble nitrate, but on warming for a few minutes on the water-bath with 1 per cent. aqueous sodium hydroxide, it is converted into hypaphorine; on acidification with nitric acid the nitrate of the latter base crystallises out. Conversely, on heating hypaphorine in methyl alcohol with sodium hydroxide and methyl iodide, the above-mentioned iodide of the ester is formed. The identity of the iodide from both sources was established by a melting-point determination of their mixture, and by solubility determinations:

100 grams of water at 18° dissolved 0·5015 gram of iodide from tryptophan.

100 grams of water at 18° dissolved 0·501 gram of iodide from hypaphorine.

Hypaphorine from the above Iodide.

By hydrolysis with sodium hydroxide, as described above, the iodide of the ester yielded hypaphorine, which was isolated as the nitrate. It is important to use only dilute alkali, for even then the odour of trimethylamine can be observed. On recrystallisation from hot water the nitrate melted somewhat indefinitely at 215—220°:

0·1112 gave 0·2230 CO_2 and 0·0618 H_2O. C=54·7; H=6·2.

$C_{14}H_{18}O_2N_2,HNO_3$ requires C=54·4; H=6·15 per cent.

The identity of the synthetic and the natural base was further established by a determination of the rotatory power of the former.

A solution of 0·299 gram of the nitrate, made up with ammonia and water to 18 c.c., gave, in a 2-dcm. tube, α_D +2·50° for

the base, whence $[\alpha]_D + 94.7°$. Greshoff found $[\alpha]_D$ 91—93° for the natural base.

The close relationship of hypaphorine to tryptophan is also expressed by several qualitative reactions; both substances have reducing properties, and, as already stated by Greshoff, hypaphorine reduces gold chloride, potassium permanganate, and ferric salts in the cold. A more characteristic and very delicate reaction which both substances have in common is that of Adamkiewicz, as modified by Hopkins and Cole, namely, an intense violet coloration on the addition of glyoxylic and sulphuric acids. On the other hand, a solution of hypaphorine is readily distinguished from a tryptophan solution by the fact that, since hypaphorine is not an amino-acid, it does not give Ruhemann's reaction with triketohydrindene hydrate (Trans., 1910, **97**, 1446; compare Abderhalden and Schmidt, *Zeitsch. physiol. Chem.*, 1911, **72**, 37).

In spite of similarity in structure, the oxidation of hypaphorine with ferric chloride proceeds quite differently from that of tryptophan. When treated according to Hopkins and Cole's method, the latter substance readily yields β-indolealdehyde, but in several experiments we could obtain from hypaphorine only a minute quantity of a substance, insufficient for complete identification. This substance, on sublimation under greatly diminished pressure, yielded crystals closely resembling those of β-indolealdehyde (similarly sublimed), but melting indefinitely about 10° lower. Oxidation experiments with hydrogen peroxide, with and without a ferrous salt as catalyst, were likewise unsuccessful.

The methylation of tryptophan also greatly changes the behaviour of the substance with sodium hydroxide, so that hypaphorine, unlike its parent substance, readily decomposes into indole and trimethylamine.

Organic Chemical Laboratory, University of Utrecht, Holland.

Chemical Laboratory, Goldsmiths' College, New Cross, S.E.

CCXXXV.—*Dihydroxydihydrindamine and its Resolution into Optically Active Components.*

By William Jackson Pope and John Read.

When an externally compensated alkyl halogen compound condenses with ammonia to form a secondary amine the reaction may conceivably proceed in two distinct kinds of way. The resulting

secondary base may contain (1) two enantiomorphously similar alkyl groups, or (2) two enantiomorphously related alkyl groups; in case (1) the secondary amine would be externally compensated, and in case (2) it would be internally compensated. Apparently no reaction of this kind has been hitherto examined, although it is one of some little importance in connexion with the mode in which chemical change occurs between optically active substances. At first sight it might appear probable that, in the condensation referred to, both the externally compensated and the internally compensated secondary amine would be produced in approximately equal proportion; on the other hand, however, it is generally recognised that reaction between alkyl halogen compounds and ammonia is modified by steric hindrance, and it may be suggested as not impossible that steric hindrance might operate to different degrees as between two enantiomorphously similar and two enantiomorphously related molecules. If some modifying cause resembling steric hindrance were operative the externally compensated and the internally compensated secondary amine would be produced in different proportion.

For the purpose of elucidating this question we have examined the conversion of externally compensated bromohydroxyhydrindene,

$C_6H_4{<}{}^{\text{—}CH_2\text{—}}_{CH(OH)}{>}CHBr$, into

$$C_6H_4{<}{}^{\text{—}CH_2\text{—}}_{CH(OH)}{>}CH{\cdot}NH{\cdot}CH{<}{}^{\text{—}CH_2\text{—}}_{CH(OH)}{>}C_6H_4,$$

the secondary amine, dihydroxydihydrindamine.

Experimental.

Externally Compensated Bromohydroxyhydrindene,

$$C_6H_4{<}{}^{\text{—}CH_2\text{—}}_{CH(OH)}{>}CHBr.$$

This substance was prepared by Krämer and Spilker (*Ber.*, 1890, **23**, 3276) by the continued boiling of dibromohydrindene with dilute alcohol. This process being rather tedious and unsatisfactory, we have devised the following method for preparing bromohydroxyhydrindene, which rapidly furnishes a 70 per cent. yield of the pure substance.

Indene is well agitated with bromine water, which it immediately decolorises, and further quantities of bromine water are added until the colour is no longer discharged after prolonged shaking; in order to reduce the volume of aqueous solution used, the later quantities of bromine may be added in aqueous potassium bromide solution. The indene becomes converted into a pasty, white, crystalline mass, from which the aqueous solution is poured off, and which is then

treated with light petroleum; the latter solvent extracts the oily impurity, and leaves a colourless, hard, crystalline product. On evaporating the petroleum from the extract a heavy, brown oil remains, which on repeated boiling with successive quantities of water yields a further quantity of bromohydroxyhydrindene. After crystallisation from aqueous alcohol, the pure substance is obtained in long, colourless needles, melting at 128—129°; on spontaneous evaporation of its solution in ethyl acetate, it is deposited in colourless, pseudohexagonal crystals, of which Mr. Arthur Hutchinson, M.A., has kindly furnished the following description:

"Crystal system: monosymmetric—$a : b : c = 3{\cdot}2080 : 1 : 2{\cdot}4615$; $\beta = 60°0'$.

Forms observed: $a\{100\}$, $c\{001\}$, $x\{\bar{1}01\}$, $y\{\bar{2}01\}$, and $v\{\bar{1}11\}$.

The following angular measurements were obtained:

	Measured.	Calculated.
$ac = 100 : 001$	60° 0′	—
$cx = 001 : \bar{1}01$	47 4	47° 9
$cy = 001 : \bar{2}01$	79 59	80 4
$ay = \bar{1}00 : \bar{2}01$	39 56	—
$xv = \bar{1}01 : \bar{1}11$	66 58	—
$av = \bar{1}00 : \bar{1}11$	83 34	83 22

The crystals are doubly terminated prisms from 5 to 10 mm. long and from 1 to 3 mm. thick. They are elongated along the diad axis, and resemble in habit crystals of the mineral epidote. The prisms a, c, and y are always present, and usually equally developed. The faces x occur but seldom, and are very narrow. The only terminal planes observed are those belonging to the form v. There is a highly perfect cleavage parallel to $c\{001\}$, and a less perfect, somewhat fibrous, cleavage parallel to $a\{100\}$. The obtuse bisectrix coincides with the diad axis. The acute bisectrix is almost normal to $a\{100\}$, and a characteristic interference figure, showing strong horizontal dispersion and an axial angle in air of approximately 52°, can be seen through these faces."

It will be noted that in the production of bromohydroxyhydrindene from indene two carbon atoms in the molecule become asymmetric, so that the former substance should exist in two externally compensated modifications. The crystalline substance just described is, however, certainly uniform, and thus can only represent one of the two possible externally compensated isomerides. We have obtained no evidence of the formation of an isomeride during the above preparation, although it is, of course, quite possible that such an isomeride may be present in the oily material formed.

Hydroxyhydrindamine and Dihydroxydihydrindamine.

Hydroxyhydrindamine, $C_6H_4<\genfrac{}{}{0pt}{}{-CH_2-}{CH(OH)}>CH\cdot NH_2$, and dihydroxydihydrindamine, $\left(C_6H_4<\genfrac{}{}{0pt}{}{-CH_2-}{CH(OH)}>CH\right)_2NH$, were prepared by Spilker (*Ber.*, 1893, **26**, 1542) by treating bromohydroxyhydrindene with alcoholic ammonia in the cold. This method is, however, conveniently replaced by the following process for preparing the two substances.

Bromohydroxyhydrindene (200 grams) is shaken mechanically in a stoppered Winchester bottle with ammonia (D 0·880; 800 grams); a clear solution first results, and this soon begins to deposit the secondary amine. After agitation for about two days the product is exposed in open basins until most of the ammonia has volatilised; the crude secondary base is then collected, and well washed with cold water. The filtrate and the washings are preserved, to be worked up for the preparation of the primary amine, which they contain in the form of hydrobromide.

Externally Compensated Dihydroxydihydrindamine,

$$C_6H_4<\genfrac{}{}{0pt}{}{-CH_2-}{CH(OH)}>CH\cdot NH\cdot CH<\genfrac{}{}{0pt}{}{-CH_2-}{CH(OH)}>C_6H_4.$$

The crude secondary amine (70 grams), prepared as above described, melts at about 160°; it is dissolved in hydrochloric acid, precipitated with ammonia, and then, after collection, crystallised from alcohol. The several fractions obtained in this way consist of small, white, feathery needles, and melt rather indefinitely at about 183°; they evidently represent the substance obtained by Spilker (*loc. cit.*), which melted at 186°.

On repeatedly extracting the substance melting at 183° with boiling ethyl acetate and recrystallising the sparingly soluble residue from boiling alcohol, a product is obtained which crystallises in small, glistening needles, and melts at 205°. This substance constitutes by far the larger proportion of the whole crude secondary amine; it is consequently to be concluded that the secondary amine now described melts at 205°, but, in the crude condition, is contaminated with some other substance which is not easily removed by recrystallisation, and which depresses the melting of the amine.

Dihydroxydihydrindamine d-*Camphor-β-sulphonate.*

The method just above indicated for preparing the pure externally compensated dihydroxydihydrindamine by extraction with ethyl

acetate and crystallisation of the residue from alcohol is inconvenient, and furnishes a very poor yield of the pure substance; the following process is much more satisfactory. The crude secondary amine melting at about 183° is dissolved in an alcoholic solution of the equivalent amount of *d*-camphor-β-sulphonic acid, and the alcoholic solution evaporated until crystallisation occurs. The white, crystalline mass of fine needles thus obtained is further purified by crystallisation from hot water, and then treated with ammonia to liberate the base; the secondary amine thus obtained is the pure externally compensated substance, melting at 205°.

ddll-*Dihydroxydihydrindamine Platinichloride.*

The externally compensated base melting at 205° yields the platinichloride when treated with platinic chloride in hydrochloric acid solution; this substance separates from hot water in glistening, orange-yellow scales, melting at 211°. It is sparingly soluble in cold water, and dissolves readily in alcohol:

0·2739 gave 0·0548 Pt. Pt = 20·01.

$C_{36}H_{38}O_4N_2,H_2PtCl_6$ requires Pt = 20·08 per cent.

Attempts to obtain the Internally Compensated or dl-*Dihydroxydihydrindamine.*

The mother liquors obtained from the separation of the above-described *d*-camphor-β-sulphonate and from the ethyl acetate treatment of the original crude dihydroxydihydrindamine yield on prolonged fractional crystallisation a small proportion of a substance which is more soluble in the usual solvents than the secondary amine melting at 205°. It crystallises in colourless needles, and melts fairly sharply at 178°. The following analysis was made:

0·0862 gave 0·2431 CO_2 and 0·0543 H_2O. C = 76·91; H = 7·05.

$C_{18}H_{19}O_2N$ requires C = 76·82; H = 6·81 per cent.

The platinichloride of this substance was obtained as a yellow oil, which could not be caused to solidify.

From the facts described above it appears legitimate to conclude that the externally compensated secondary base melting at 205° is accompanied by a small proportion of the internally compensated isomeride, and that the latter melts at about 178°.

The Resolution of Externally Compensated Dihydroxydihydrindamine.

It has been shown above that on crystallising dihydroxydihydrindamine with *d*-camphor-β-sulphonic acid a partly racemic salt is formed, and that no resolution of the externally compensated base

can be effected by crystallisation with the optically active acid under ordinary conditions.

On crystallising the secondary amine melting at about 183° from an aqueous solution of the corresponding amount of *d*-α-bromocamphor-π-sulphonic acid, a partly crystalline mass is deposited, which, after separation, is obtained in small, opaque nodules by crystallisation from hot water; the salt is very difficult to purify, owing mainly to the ease with which hydrolytic dissociation occurs, but the purification is facilitated by crystallisation from boiling ethyl acetate containing a little alcohol. The salt ultimately obtained yields, when treated with ammonia, the dextro-amine contaminated with some amount of the lævo-isomeride.

By prolonged fractional crystallisation of the crude bromocamphorsulphonate from ethyl acetate, it can be resolved into the sparingly soluble *d*-dihydroxydihydrindamine *d*-α-bromocamphor-π-sulphonate and the more readily soluble *l*-dihydroxydihydrindamine *d*-α-bromocamphor-π-sulphonate. The difference in solubility between these two salts is, however, so slight that no large proportion of the two active secondary amines can be separated in the form of the pure salts. It is most convenient to effect a rough separation by allowing about two-thirds of the salt to crystallise from ethyl acetate, and then to liberate the crude *d*-base from the sparingly soluble salt, and the crude *l*-isomeride from the mother liquors by treatment with ammonia; the optically active secondary amines are much less soluble in alcohol than is the externally compensated isomeride, and the former may easily be obtained in a state of purity by crystallising the crude bases from this solvent; thus, in one case, the mother liquors yielded a base exhibiting the specific rotatory power, $[\alpha]_{\mathrm{Hg\ green}}$ $-52{\cdot}6°$; after one crystallisation from alcohol this value was found to be $-95{\cdot}7°$, and a second crystallisation raised the specific rotatory power to that of the pure *l*-amine, namely, $-100{\cdot}0°$.

d- *and* l-*Dihydroxydihydrindamine*,

$$\left[C_6H_4{<}{\begin{smallmatrix}CH_2\\CH(OH)\end{smallmatrix}}{>}CH\right]_2NH.$$

The *d*- and *l*-dihydroxydihydrindamines are sparingly soluble in boiling alcohol, and separate therefrom in long, silky needles, melting at 223°; on crystallising equal quantities of the two isomerides together from alcohol, the externally compensated substance melting at 205° is obtained. This completes the proof that the compound described above (p. 2074) is the pure externally compensated secondary base:

0·0888 of *l*-base gave 0·2503 CO_2 and 0·0556 H_2O. C=76·87; H=7·01.

$C_{18}H_{19}O_2N$ requires C=76·82; H=6·81 per cent.

The very sparing solubility of these bases in the ordinary solvents renders it difficult to determine their rotation constants in neutral solvents; further, the substances are so feebly basic that their salts are hydrolytically dissociated with great readiness, and it is consequently difficult to ensure the purity of the solid salts. The following determinations of rotatory power were therefore made by dissolving known weights of the bases in the calculated quantities of hydrochloric acid, making up to 30·0 c.c. with water, and examining at 18° in 4-dcm. tubes.

l-*Dihydroxydihydrindamine.*

Weight taken.		Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
0·0990 gram	α	− 1·32°	− 1·14°	− 1·10°
	[α]	100·0	86·4	83·3
	[M]	281·0	243·0	234·0
0·6022 gram	α	7·88	6·78	6·53
	[α]	98·1	84·4	81·3
	[M]	276·0	237·0	229·0

d-*Dihydroxydihydrindamine.*

0·1037 gram	α	+ 1·38°	+ 1·19°	+ 1·15°
	[α]	99·8	86·1	83·2
	[M]	281·0	242·0	234·0

The mean rotatory dispersions for the basic ion in aqueous solution are thus, for Hg_{green}/Na_{yellow} = 1·200, and for Hg_{yellow}/Na_{yellow} = 1·037.

d- *and* l-*Dihydroxydihydrindamine Platinichloride,* $[(C_9H_9O)_2NH]_2,H_2PtCl_6$.

The platinichlorides of the active bases separate from hot water, in which they are moderately soluble, in glistening, orange needles, melting at 185°; the solutions must be kept slightly acidified with hydrochloric acid in order to prevent precipitation of the base owing to hydrolytic dissociation. The salts are readily soluble in alcohol:

0·3013 gave 0·0602 Pt. Pt=19·98.

$C_{36}H_{38}O_4N_2,H_2PtCl_6$ requires Pt=20·08 per cent.

The following determinations of rotatory powers were made by dissolving 0·1508 gram of *d*-hydroxydihydrindamine platinichloride

in water with addition of a drop of dilute hydrochloric acid, making up to 30 c.c. with water, and examining in a 4-dcm.-tube at 18°.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	+ 1·12°	+ 0·95°	+ 0·93°
$[\alpha]$	55·7	47·2	46·3
$[M]/2$	271·0	230·0	225·0

The rotatory dispersions are, for $Hg_{green}/Na_{yellow} = 1{\cdot}203$, and for $Hg_{yellow}/Na_{yellow} = 1{\cdot}019$. These values are in good agreement with those quoted above for the basic ions in hydrochloric acid solutions.

l-*Dihydroxydihydrindamine* d-*α-Bromocamphor-π-sulphonate*, $(C_9H_9O)_2NH,C_{10}H_{14}OBr{\cdot}SO_3H,H_2O$.

This salt is conveniently obtained in a state of high purity by crystallising the *l*-base with the corresponding amount of the *d*-acid from water, and recrystallising the product from water slightly acidified with hydrochloric acid; it forms opaque clusters of minute, colourless needles, melting at 210—215°:

0·0953 gave 0·1884 CO_2 and 0·0512 H_2O. C = 55·07; H = 6·14.

$C_{28}H_{36}O_7NBrS$ requires C = 55·08; H = 5·95 per cent.

0·2731 lost 0·0078 at 100°. H_2O = 2·86; $1H_2O$ requires 2·95.

The following determinations of rotatory power were made with the air-dried salt (1) in alcoholic solution, and (2) in water, with the addition of a drop of dilute hydrochloric acid; the weight taken was made up to 30 c.c., and the solution examined in a 4-dcm. tube at 18°.

Weight taken.		Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
0·1522 gram	α	+ 0·88°	+ 0·74°	+ 0·69°
in alcohol	$[\alpha]$	43·4	36·5	34·0
	$[M]$	265·0	223·0	207·0

Rotatory dispersions: $Hg_{green}/Na_{yellow} = 1{\cdot}276$; $Hg_{yellow}/Na_{yellow} = 1{\cdot}074$.

0·1020 gram	α	+ 0·13°	+ 0·09°	+ 0·08°
in water	$[\alpha]$	9·6	6·6	5·9
	$[M]$	59·0	40·0	36·0
Calculated ...	$[M]$	65·4	52·3	44·5

Rotatory dispersions: $Hg_{green}/Na_{yellow} = 1{\cdot}627$; $Hg_{yellow}/Na_{yellow} = 1{\cdot}119$. The calculated values for the molecular rotatory powers are derived from the values observed for the hydrochloric acid solutions of the base and of aqueous solutions of the ammonium salt of the acid; the observed values are low, probably owing to the presence of a slight excess of the base produced by hydrolytic dissociation.

l-*Dihydroxydihydrindamine* l-*a-Bromocamphor-π-sulphonate.*

This salt is prepared in a state of purity in the same manner as the one previously described; it forms long, silky, colourless needles, melting at 230—232°, and is easily soluble in alcohol or ethyl acetate, and sparingly so in water:

0·0976 gave 0·1959 CO_2 and 0·0530 H_2O. C=54·71; H=6·08.

$C_{28}H_{36}O_7NBrS$ requires C=55·05; H=5·95 per cent.

0·2360 lost 0·0071 at 100°. H_2O=3·01; $1H_2O$ requires 2·95.

The following determinations of rotatory power were made in the same way as those quoted for the previous salt:

Weight taken.		Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
0·1525 gram	α	− 1·69°	− 1·41°	− 1·34°
in alcohol	[α]	83·1	69·3	65·9
	[M]	507·0	423·0	402·0

Rotatory dispersions: Hg_{green}/Na_{yellow} = 1·261; Hg_{yellow}/Na_{yellow} = 1·052.

0·1000 gram	α	− 1·37°	− 1·18°	− 1·10°
in water	[α]	102·8	88·5	82·5
	[M]	628·0	540·0	503·0
Calculated......	[M]	628·0	538·0	513·0

Rotatory dispersions: Hg_{green}/Na_{yellow} = 1·246; Hg_{yellow}/Na_{yellow} = 1·073. The calculated values for the molecular rotatory powers were derived in the manner indicated for the previously described salt.

Externally Compensated Hydroxyhydrindamine,

$$C_6H_4<\begin{matrix}CH_2\\CH(OH)\end{matrix}>CH\cdot NH_2.$$

In order to obtain this primary amine it is convenient to evaporate the aqueous mother liquors containing the hydrobromide, referred to on p. 2074, to dryness on the water-bath, then to dissolve in a little boiling water, and to add about twice the calculated quantity of concentrated aqueous potassium hydroxide after partial cooling. The crude amine separates as a pale yellow, crystalline precipitate, and is obtained in a state of purity by crystallisation from boiling benzene; it forms glistening, white scales, melting at 128—129°, and is quite stable in the air. It does not appear to absorb carbon dioxide and moisture from the atmosphere in the manner mentioned by Spilker (*loc. cit.*). The hydrochloride is precipitated from concentrated solutions by excess of hydrochloric acid as a white, crystalline mass; the *platinichloride* crystallises from hot water in orange needles, melting at 232°, and is readily soluble in alcohol:

0·3067 gave 0·0845 Pt. Pt=27·55.

$C_{18}H_{22}O_2N_2,H_2PtCl_6$ requires Pt=27·56 per cent.

The resolution of this amine into its optically active components can be effected by crystallisation with *d*-α-bromocamphor-π-sulphonic acid, and will shortly be described.

In the treatment of externally compensated bromohydroxyhydrindene with concentrated aqueous ammonia solution in the manner described above, it is converted quantitatively into a mixture of the secondary base and the primary base, hydroxyhydrindamine; in one large preparation the former product was obtained in a 55 per cent. yield, and the primary amine in a 45 per cent. yield, no unchanged material being recovered.

It is to be supposed that the first action of the ammonia is to convert bromohydroxyhydrindene into the primary externally compensated amine, hydroxyhydrindamine, and that by the action of bromohydroxyhydrindene the latter substance becomes partly converted into the secondary dihydroxydihydrindamine. We have shown that the secondary amine melting at 183° consists mainly of the externally compensated base melting at 205°, and contains but a small proportion of an isomeride melting at 178°, this being probably the internally compensated secondary amine; it therefore follows that in the formation of the secondary base condensation occurs between the alkyl bromide and hydroxyhydrindamine, which are enantiomorphously similar in molecular configuration, and that very little tendency is exhibited for condensation to occur between the hydroxyhydrindyl radicles of enantiomorphously dissimilar configurations. Representing the hydroxyhydrindyl radicle,

$$C_6H_4{<}{\begin{matrix}CH_2\\CH(OH)\end{matrix}}{>}CH,$$

by the symbol R, the reaction which occurs to a preponderating extent is represented by the equations:

$$d\text{-}R{\cdot}NH_2 + d\text{-}RBr = (d\text{-}R)_2NH + HBr$$

and

$$l\text{-}R{\cdot}NH_2 + l\text{-}RBr = (l\text{-}R)_2NH + HBr.$$

The alternative reactions represented by the equations:

$$d\text{-}R{\cdot}NH_2 + l\text{-}RBr = (d\text{-}R)(l\text{-}R)NH + HBr$$

and

$$l\text{-}R{\cdot}NH_2 + d\text{-}RBr = (d\text{-}R)(l\text{-}R)NH + HBr$$

apparently proceed to but a very slight extent.

THE CHEMICAL LABORATORY,
THE UNIVERSITY, CAMBRIDGE.

CCXXXVI.—*Studies in Phototropy and Thermotropy. Part II. Naphthylideneamines.*

By ALFRED SENIER and ROSALIND CLARKE.

IN previous communications on certain Schiff's bases (Senier and Shepheard, Trans., 1909, **95**, 441, 1943) several of these compounds were described, some of which possessed phototropic properties, and nearly all of which were thermotropic. It was noticed that those exhibiting phototropy were all derived from salicylaldehyde, in which the substituents are in the ortho-position with respect to each other. Moreover, other investigators have shown generally that when isomerism occurs among Schiff's bases the compounds are ortho-compounds, with a few exceptions, when they are para-. This being so, it seemed interesting to continue the search for phototropy and thermotropy among compounds of this class, and, for this purpose, we have prepared and studied a number of new bases derived from 2-hydroxy-α-naphthaldehyde, in which the naphthalene nucleus takes the place of the benzene ring in salicylaldehyde. None of the bases described proved to be phototropic, but all show thermotropy in greater or less degree. At the "lower temperature" (*loc. cit.*) all become paler in colour, and at the "higher temperature" deeper; orange becomes yellow, and yellow, orange, or, in the case of the aminophenol derivatives, red.

The bases, naphthylideneamines, were prepared by bringing together molecular proportions of the aldehyde and amine in alcoholic solution, and recrystallising the crystals thus obtained from that medium or from methyl alcohol.

2-Hydroxy-α-naphthylidene-o-chloroaniline,

$$OH\cdot C_{10}H_6\cdot CH\colon N\cdot C_6H_4Cl,$$

crystallises from alcohol in yellow needles, which are sparingly soluble in ether, but readily so in acetone, chloroform, or light petroleum. It melts at 144·5° (corr.):

0·4860 gave 21·0 c.c. N_2 (moist) at 15° and 733 mm. N = 4·88.

$C_{17}H_{12}ONCl$ requires N = 4·97 per cent.

2-Hydroxy-α-naphthylidene-m-chloroaniline,

$$OH\cdot C_{10}H_6\cdot CH\colon N\cdot C_6H_4Cl,$$

occurs in orange-yellow needles when crystallised from alcohol or light petroleum. It is sparingly soluble in ether, readily so in benzene, chloroform, or acetone, and melts at 116—117° (corr.):

0·5222 gave 23·7 c.c. N_2 (moist) at 16·5° and 748 mm. N = 5·20.

$C_{17}H_{12}ONCl$ requires N = 4·97 per cent.

2-*Hydroxy-α-naphthylidene*-p-*chloroaniline*,

$OH \cdot C_{10}H_6 \cdot CH \colon N \cdot C_6H_4Cl$,

consists of yellow, silky needles, which dissolve sparingly in ether, but are readily soluble in chloroform, acetone, benzene, or light petroleum. It melts at 158—159° (corr.):

0·5558 gave 23·4 c.c. N_2 (moist) at 14° and 766 mm. N = 4·99.
$C_{17}H_{12}ONCl$ requires N = 4·97 per cent.

2-*Hydroxy-α-naphthylidene*-o-*bromoaniline*,

$OH \cdot C_{10}H_6 \cdot CH \colon N \cdot C_6H_4Br$,

was obtained in yellow needles, which dissolve readily in the usual solvents. It melts at 150° (corr.):

0·5546 gave 19·9 c.c. N_2 (moist) at 14° and 780 mm. N = 4·33.
$C_{17}H_{12}ONBr$ requires N = 4·30 per cent.

2-*Hydroxy-α-naphthylidene*-m-*bromoaniline*,

$OH \cdot C_{10}H_6 \cdot CH \colon N \cdot C_6H_4Br$,

crystallises in orange-yellow needles. Its behaviour towards the usual solvents is similar to that of the ortho-compound. It melts at 144° (corr.):

0·5016 gave 17·8 c.c. N_2 (moist) at 13·5° and 778 mm. N = 4·28.
$C_{17}H_{12}ONBr$ requires N = 4·30 per cent.

2-*Hydroxy-α-naphthylidene*-p-*bromoaniline*,

$OH \cdot C_{10}H_6 \cdot CH \colon N \cdot C_6H_4Br$,

separates, in the first instance, in yellow leaflets, and, when recrystallised from alcohol, in pale yellow, silky needles. It dissolves readily in benzene, chloroform, acetone, or light petroleum, and less so in ether. It melts at 166·5° (corr.):

0·4930 gave 17·7 c.c. N_2 (moist) at 13° and 769 mm. N = 4·30.
$C_{17}H_{12}ONBr$ requires N = 4·30 per cent.

2-*Hydroxy-α-naphthylidene*-m-*nitroaniline*,

$OH \cdot C_{10}H_6 \cdot CH \colon N \cdot C_6H_4 \cdot NO_2$,

occurs in orange-red needles. It dissolves readily in alcohol, benzene, or chloroform, more sparingly in light petroleum, and melts at 178·5—179·5° (corr.):

0·3331 gave 27 0 c.c. N_2 (moist) at 17° and 772 mm. N = 9·56.
$C_{17}H_{12}O_3N_2$ requires N = 9·59 per cent.

2-*Hydroxy-α-naphthylidene*-o-*aminophenol*,

$OH \cdot C_{10}H_6 \cdot CH \colon N \cdot C_6H_4 \cdot OH$,

separates in brown crystals, which are somewhat soluble in the usual solvents, but do not readily crystallise from them. It melts and decomposes at 248—250° (corr.):

0·4777 gave 22·2 c.c. N_2 (moist) at 19° and 765 mm. N = 5·38.
$C_{17}H_{13}O_2N$ requires N = 5·32 per cent.

*2-Hydroxy-α-naphthylidene-*m*-aminophenol*,

$$OH\cdot C_{10}H_6\cdot CH:N\cdot C_6H_4\cdot OH,$$

separated in yellow needles, which were recrystallised from alcohol. It dissolves readily in most solvents, with the exception of light petroleum, in which it is almost insoluble. It begins to melt and decompose at 221° (corr.):

0·4334 gave 19·4 c.c. N_2 (moist) at 22° and 765 mm. N=5·11.

$C_{17}H_{13}O_2N$ requires N=5·32 per cent.

*2-Hydroxy-α-naphthylidene-*p*-aminophenol*,

$$OH\cdot C_{10}H_6\cdot CH:N\cdot C_6H_4\cdot OH,$$

at first appeared as yellow needles, which became darker on successive recrystallisations from alcohol. It melts and decomposes at 229·5° (corr.):

0·5384 gave 26·3 c.c. N_2 (moist) at 15° and 750 mm. N=5·65.

$C_{17}H_{13}O_2N$ requires N=5·32 per cent.

2-Hydroxy-α-naphthylidene-o-anisidine,

$$OH\cdot C_{10}H_6\cdot CH:N\cdot C_6H_4\cdot OMe,$$

occurs as bright yellow, silky crystals, which dissolve readily in the usual solvents. It melts at 178·5° (corr.):

0·5543 gave 23·8 c.c. N_2 (moist) at 9° and 779 mm. N=5·29.

$C_{18}H_{15}O_2N$ requires N=5·05 per cent.

*2-Hydroxy-α-naphthylidene-*m*-anisidine*,

$$OH\cdot C_{10}H_6\cdot CH:N\cdot C_6H_4\cdot OMe,$$

forms yellow needles, which dissolve readily in the usual solvents, and melt at 107·5—108·5 (corr.):

0·4468 gave 19·3 c.c. N_2 (moist) at 17° and 762 mm. N=5·03.

$C_{18}H_{15}O_2N$ requires N=5·05 per cent.

*2-Hydroxy-α-naphthylidene-*p*-anisidine*,

$$OH\cdot C_{10}H_6\cdot CH:N\cdot C_6H_4\cdot OMe,$$

crystallises in clusters of long, yellow, silky needles, which are readily soluble in the usual solvents, and melt at 111—112° (corr.):

0·4798 gave 20·3 c.c. N_2 (moist) at 11·5° and 766 mm. N=5·08.

$C_{18}H_{15}O_2N$ requires N=5·05 per cent.

2-Hydroxy-α-naphthylidene-o-aminobenzoic acid,

$$OH\cdot C_{10}H_6\cdot CH:N\cdot C_6H_4\cdot CO_2H,$$

separated in orange-yellow crystals. It is sparingly soluble in methyl alcohol, more readily so in benzene, ethyl acetate, chloroform, toluene, or light petroleum, and melts at 227·5° (corr.):

0·5014 gave 20·8 c.c. N_2 (moist) at 20° and 766 mm. N=4·78.

$C_{18}H_{13}O_3N$ requires N=4·81 per cent.

*2-Hydroxy-α-naphthylidene-*m*-aminobenzoic acid*,

$$OH\cdot C_{10}H_6\cdot CH:N\cdot C_6H_4\cdot CO_2H,$$

occurs in yellow needles, which are sparingly soluble in benzene or light petroleum, but readily so in alcohol or chloroform. It melts and decomposes at 281·5° (corr.):

0·3417 gave 14·0 c.c. N_2 (moist) at 19° and 767 mm. N = 4·76.

$C_{18}H_{13}O_3N$ requires N = 4·81 per cent.

2-*Hydroxy-α-naphthylidene*-p-*aminobenzoic acid*,

$OH\cdot C_{10}H_6\cdot CH\colon N\cdot C_6H_4\cdot CO_2H$,

separates in yellow crystals, which are sparingly soluble in alcohol, more readily so in chloroform, benzene, or methyl alcohol, and insoluble in light petroleum. It melts and decomposes at 298° (corr.):

0·4621 gave 19·2 c.c. N_2 (moist) at 27° and 771 mm. N = 4·67.

$C_{18}H_{13}O_3N$ requires N = 4·81 per cent.

2-*Hydroxy-α-naphthylidene-o-4-xylidine*,

$OH\cdot C_{10}H_6\cdot CH\colon N\cdot C_6H_3Me_2$,

crystallises in yellow needles, dissolves readily in the usual solvents, and melts at 125·5° (corr.):

0·5746 gave 24·0 c.c. N_2 (moist) at 10° and 763 mm. N = 5·02.

$C_{19}H_{17}ON$ requires N = 5·09 per cent.

2-*Hydroxy-α-naphthylidene*-m-4-*xylidine*,

$OH\cdot C_{10}H_6\cdot CH\colon N\cdot C_6H_3Me_2$,

forms yellow needles, melting at 157° (corr.). Its behaviour towards solvents is similar to that of the ortho-compound:

0·4637 gave 19·8 c.c. N_2 (moist) at 15·5° and 762 mm. N = 5·01.

$C_{19}H_{17}ON$ requires N = 5·09 per cent.

2-*Hydroxy-α-naphthylidene*-p-*xylidine*,

$OH\cdot C_{10}H_6\cdot CH\colon N\cdot C_6H_3Me_2$,

was obtained in yellow crystals, which dissolve in the usual solvents. It melts at 108·5—109·5° (corr.):

0·4874 gave 21·1 c.c. N_2 (moist) at 18° and 750 mm. N = 4·94.

$C_{19}H_{17}ON$ requires N = 5·09 per cent.

2-*Hydroxy-α-naphthylidene-ψ-cumidine*,

$OH\cdot C_{10}H_6\cdot CH\colon N\cdot C_6H_2Me_3$,

separates in yellow needles, which are readily soluble in alcohol, chloroform, benzene, or light petroleum, and melt at 146—147° (corr.):

0·5996 gave 25·2 c.c. N_2 (moist) at 15° and 759 mm. N = 4·92.

$C_{20}H_{19}ON$ requires N = 4·84 per cent.

University College,
Galway.

CCXXXVII.—*Isomeric Acetaldehydephenylhydrazones.*

By Ernyst Graham Laws and Nevil Vincent Sidgwick.

After preliminary work by Emil Fischer, and Bamberger and Pemsel, the isomeric acetaldehydephenylhydrazones were carefully investigated by Lockemann and Liesche (*Annalen*, 1905, **342**, 14), who showed that the α-form was converted into the β- by acids, and that the β- was transformed into the α-modification by alkalis, and, further, that it was not necessary for the hydrazone to pass into solution in the course of these transformations. These results are quite exceptional, and it was thought worth while to re-investigate these substances.

Experimental.

Preparation of the Hydrazone.

Lockemann and Liesche prepared the hydrazone in light petroleum solution, but a purer yield is obtained by using aqueous alcohol as solvent. One hundred and twenty c.c. of alcohol were mixed with 20 c.c. of water in a flask fitted with cork and upright condenser, and placed in a trough of cold water. Thirty grams of acetaldehyde were poured in, and the mixture shaken. Sixty grams of phenylhydrazine, purified by recent distillation in a vacuum, were then added in portions, the whole being shaken after each addition, and time being given to cool before adding the next. (If the mixture becomes hot, decomposition sets in, and the preparation is ruined.) Crystallisation can be induced by sowing or scratching, and the liquid should be shaken until small crystals are distributed throughout the whole mass. The apparatus is left for an hour or so to cool completely. The material is then collected, and washed with a little aqueous alcohol. The product is pure white, and does not become discoloured in air for some time. In one experiment, using the above quantities, the product when dry weighed 56 grams.

The hydrazone obtained in this way had in different experiments melting points varying between 56° and 80°, the value depending no doubt on the relative proportions of the two isomerides present. The hydrazone decomposes in air, very slowly at first, but afterwards more rapidly, becoming finally a dark brown oil. It is best stored in a vacuum over potassium hydroxide or phosphoric oxide.

Preparation of the Isomerides.

α-Form.—After recrystallisation from aqueous alcohol containing a trace of potassium hydroxide, the product invariably had a high

melting point—from 80° to 98°—the figures depending partly no doubt on the purity of the product. The highest values were obtained when the hydrazone was prepared from phenylhydrazine which had been freshly distilled, or when the product was distilled in a vacuum previous to crystallisation from alkaline alcohol; then the melting point was always above 93°, and generally 98°. This effect was always produced by a single crystallisation. The temperature to which the liquid was heated before cooling, or the time for which the heating was continued, seemed to have no effect on the transformation. The concentration of the alkali was not important provided that sufficient was present to make the liquid definitely alkaline.

β-Form.—Recrystallisation of the product from aqueous alcohol containing a trace of sulphur dioxide gave, as Lockemann and Liesche state, the β-form, melting at 56°. Great care is necessary here, for if the concentration of the acid is too great, or if the solution is heated to too high a temperature or for too long a time, decomposition sets in, and nothing can be induced to crystallise out. The solution must remain straw-coloured; if it becomes definitely yellow the preparation is spoilt. The stronger acids were found by Lockemann and Liesche to be unsuited for the purpose—an impure product was always obtained owing to decomposition. If, however, the stronger acids are used at great dilution, a pure product, melting sharply at 56°, is always obtained. Rapid recrystallisation from 75 per cent. aqueous alcohol containing two to three drops of hydrochloric acid was the method generally adopted for the preparation of the β-form.

Transformation of the Isomerides.

By recrystallisation from acidic aqueous alcohol, by immersion in aqueous acids, and by leaving the solid in an atmosphere of sulphur dioxide, the α-form (m. p. 98°) and products of intermediate melting point are converted into the β-form (m. p. 56°).

By recrystallisation from alkaline aqueous alcohol, by immersion in aqueous alkalis, and by keeping in an atmosphere of ammonia gas, the melting point of the β-form is raised considerably, although this reverse change does not always proceed sufficiently to give the pure α-product melting at 98°.

These experiments confirmed the most important points in Lockemann and Liesche's paper. In particular, it was noted that where the transformation was caused by aqueous and gaseous alkali or acid, the crystals were quite unaltered during the process, and no change in their appearance could be detected even under the microscope. The action of alkalis takes place much more slowly and often less completely than the opposite action of acids. Drying with

phosphoric oxide greatly retards the change in the case of sulphur dioxide, but drying with potassium hydroxide seems to be without effect on the action of ammonia in causing the reverse transformation.

Effect of Fusion.

Experiments in which each form was kept fused in a vacuum showed that the freezing point had not undergone any appreciable change after one hour. After six hours the freezing point of the α-form, originally 98°, had fallen to 90°, whilst that of the β-form, originally 56°, had fallen to 55°, but it was noticed that both liquids had now become discoloured.

On fusion in air the fall in freezing point and the darkening of the liquid occurred more quickly, for example, the α-form, originally fusing at 98°, melted at 55° after three hours. Working rapidly in air, two successive freezing points could be obtained with the same portion of material not differing by more than 1°.

These experiments seemed to indicate that the freezing point did not change until decomposition set in, as indicated by the darkening of the liquid.

Freezing-point Curve.—Various difficulties, due probably to the low heat of fusion of the hydrazone and to its small velocity of crystallisation, were encountered in the attempts to obtain this curve. The method finally adopted was as follows:

The mixture of α- and β-forms was made up in the required proportions in the substance tube of a Beckmann apparatus, fused completely at as low a temperature as possible, and at once withdrawn and allowed to cool in the air until crystallisation occurred. It was always stirred vigorously, so that very fine crystals were produced. The tube was then placed in position in the Beckmann apparatus, and the bath, previously regulated to a few degrees below the expected freezing point, gently heated. The substance soon became warm and more liquid. The temperature at which the last few crystals disappeared was taken. It could be determined quite accurately, for the temperature rose very slowly until all the substance had liquefied, when the rate became much greater. The solid present made the mercury in the thermometer bulb appear quite dull, but, as the last crystals dissolved, the lustre of the mercury again became visible.

This temperature is not a freezing point in the ordinary sense of the word, but a "dissolving point." The method gives the temperature at which the crystals of highest melting point dissolve in the liquid with which they are in contact. Theoretically, it should be identical with the freezing point; practically, it will tend to be above the "theoretical freezing point" (when supercooling is

nil), whereas the ordinarily determined freezing point tends to be below it.

The results obtained by this method are given in the table below:

α-Form (grams).	β-Form (grams).	α-Form, per cent.	F. p.
		Set 1.	
6·0	0·0	100	98·6°
4·5	0·5	90	92·0
3·0	1·0	75	82·2
3·0	2·0	60	75·0
2·7	3·3	45	68·0
2·0	3·0	40	56·0 *
		Set 2.	
0·0	5·0	0	56·0°
0·9	5·1	15	59·0
1·5	3·5	30	63·2
2·0	3·0	40	65·4
2·5	2·5	50	69·8
2·0	1·0	66·6	78·0
		Set 3.	
0·0	5·0	0	56·0°
0·25	4·75	5	56·8
0·5	4·5	10	57·6
1·0	4·0	20	60·0

* Inexplicable except assuming that a trace of acid was accidentally introduced.

The three sets of experiments were carried out with different preparations of the isomerides. The results are also recorded in the curve on p. 2089.

This curve indicates that the two components—the two isomerides—form a continuous series of mixed crystals (solid solutions). The curve would necessarily fall at both ends if solid solutions were not formed. So far as is known, this is the first case where this has been established, although a similar behaviour has been assumed by Hantzsch in the case of the diazonium salts and nitrophenols. The behaviour in question is due to the close similarity in properties of the two forms, which is evident from the following considerations:

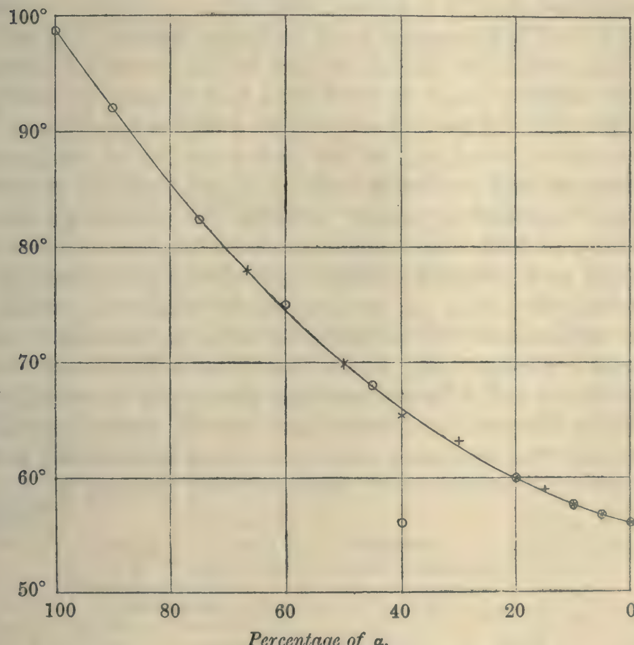
Some of the pure α- and β-forms, and also crystals of various intermediate melting points, were examined under the microscope. Irregularities in the crystals prevented exact measurements being taken, but, so far as they could be tested, they appeared to be absolutely identical. Moreover, no change could be seen, even in optical properties, while a fairly large crystal of α was being converted into β under the microscope by a drop of acid.

Again, the introduction of either isomeride will effect crystallisation of the other from its supersaturated solutions; thus crystals of the α-form when introduced into a supersaturated acid solution

of the hydrazone immediately cause the crystallisation of the β-variety, and, in the same way, the introduction of the β crystals causes the α-variety to separate out from alkaline solutions. From neutral solutions, crystals of intermediate melting point are obtained by sowing with α or β, and the melting point of the product is the same whichever be used.

Further, so far as could be determined, the two isomerides have

Freezing-point curve.



the same density, that of the α-form being 1·181, of the β-form 1·180, and of the mixed crystals 1·180.

Influence of the Solvent.

Lockemann and Liesche's conclusions on this question were not at all satisfactory. The method finally adopted in the present work was to recrystallise a fairly large quantity of each isomeride several times from each of the solvents investigated. The recrystallisations were done as rapidly as possible, and a fresh portion of solvent was used for each crystallisation, as hot solutions of the hydrazone soon begin to decompose when in contact with air. A sample of the hydrazone was reserved at each stage, and its freezing point determined by the method used in obtaining the above curve.

Solvent: Alcohol.

		Freezing point after recrystallising.			
Form.	Original f.p.	Once.	Twice.	Thrice.	Four times.
α	98°	83·0°	77·2°	73·2°	74°
β	56	58·0	74·0	76·0	—
mixed crystals	72	77·2	75·2	73·5	—
,,	68	73·6	76·4	75·0	—
,,	65	75·3	73·3	75·2	—

In each case there is a marked alteration on the first crystallisation, and then the freezing point oscillates between 73° and 77°. If the same portion of alcohol be used for the successive crystallisations, the freezing point of the α-form falls successively lower each time, whilst that of the β-form rises at first but finally falls. This behaviour is explained by the fact that a solution of the hydrazone in aqueous alcohol gradually becomes slightly acid on exposure to air. The "equilibrium values" obtained for alcohol are probably all too low, and their divergence is doubtless due to the varying amounts of acid produced in the process of each crystallisation. The experiments show that an equilibrium is reached in alcohol, but they do not indicate with certainty the value of that equilibrium.

Solvents: Benzene and Light Petroleum.—With each of these solvents the α- and β-forms remained unchanged in freezing point after three recrystallisations carried out in the above manner. Various mixtures, originally melting at points between 60° and 84°, finally gave an "equilibrium" product fusing between 82° and 83°.

Solvent: Water.

		Freezing point after crystallising.	
Form.	Original f.p.	Once.	Twice.
α	98°	81·0°	81°
β	56	80·0	81
mixed crystals	75	81·0	81
,,	71	81·5	81

Water free from air was used in these experiments, as otherwise considerable oxidation occurred. These figures indicate that the isomeric change occurs rapidly in aqueous solutions, a definite equilibrium being established in the time required for a single crystallisation.

The hydrazone was found to be volatile in steam. Steam distillation gave exactly the same results as recrystallisation from water. Whatever the freezing point of the crystals used, the product invariably had a freezing point of 80—81°.

Vacuum Distillation.

Lockemann and Liesche state that each form can be distilled in a vacuum, but give no details. In the following experiments the pressure was kept fairly constant at 20—21 mm.

β-Form.

	1st Fraction.		2nd Fraction.		3rd Fraction.	
Expt.	Collected at	Freezing point.	Collected at	Freezing point.	Collected at	Freezing point.
1	133°	56·0°	133—134°	56·3°	134—135°	56·1°
2	134	56·0	134	56·2	134—135	56·2
3	133—134	56·1	134	56·0	134—136	56·3

These results indicate that the β-form distils unchanged at 133—136°/20 mm. The distillate was a pale yellow, mobile liquid, which readily solidified in the receiver. The freezing-point determinations show that there is no appreciable difference in composition between the separate fractions.

Mixed Crystals of Intermediate Composition.—The reaction product was used for these experiments. It was purified by a single crystallisation from neutral aqueous alcohol. The following result is typical of many that were obtained with crystals of different freezing points:

Freezing point of substance used.	Fraction.	Collected at	Character.	Approx. quantity.	Freezing point of fraction.
80°	A	134—135°	Mobile, colourless, froze in receiver	5 c.c.	70°
	B	135—235°	As A at first, then as C	5 ,,	75
	C	235—237°	Viscid, deep yellow, solidified with difficulty	5 ,,	96—97

These experiments show that it is, to a certain extent, possible to separate a mixture of the isomerides by this method. The temperature remains between 130° and 140°, whilst products distil over, the freezing points of which range from 56° to 70°. In the case of the mixtures of higher freezing point, such as the above, the temperature then rises quickly through 100°, during which time very little passes over. At 235° the boiling again becomes vigorous, but the character of the distillate is very different, and the freezing point indicates that it consists mainly of the α-form.

a-Form.

The following is a typical result:

Freezing point of substance used.	Fraction.	Collected at	Character.	Approx. quantity.	Freezing point of fraction.
98°	A	135—236°	Thin at first, then viscid	2—3 c.c.	92°
	B	236—237	Viscid and yellow	12 ,,	98—99

The behaviour is qualitatively the same as that of the reaction product. The rapid rise occurs earlier in the experiment, and the main portion consists of the higher boiling fraction.

Discussion of Results.

The chief result of this work has been to confirm in more detail many of Lockemann and Liesche's statements. The freezing-point curve definitely proves that the two forms are isomorphous, and form a continuous series of mixed crystals. They have, moreover, the same density, and undergo no physical change—even in optical properties—when transformation takes place.

Lockemann and Liesche state that the β-form rises in melting point when stored in a neutral medium, and draw the conclusion that the α-variety is the stable form. This observation could not be confirmed. Alone, whether in the solid, liquid, or gaseous state, when oxidation is prevented, each isomeride seems perfectly stable; the α- and β-forms, and all intermediate mixtures of them, undergo no change whatever, but, excepting (probably) when moisture is rigidly excluded, the presence of acid causes transformation to the lower melting end of the series of mixed crystals, whilst the presence of alkali causes the opposite transformation.

The peculiarity of the isomerism is obviously connected with the very small difference in energy content, and therefore in the relative stability of the two forms. On the other hand, there can be no doubt that the α-form is more stable in presence of alkali and the β- in presence of acid, and that a trace of acid or alkali can bring about a change from one to the other, proceeding through a mass of crystals without their passing into solution. It therefore follows that there is a difference between the crystals in contact with acid and crystals in contact with alkali. This can only come about by adsorption of acid or alkali into the crystals, which causes a difference in energy greater than the difference between the two absolutely pure forms.

No trace of acid or alkali could be found in the crystals by direct experiment, but this is not a very serious objection. The total

quantity of acid or alkali present is very small indeed, and the partition-coefficient would doubtless be greatly in favour of the water, of which there is a much larger quantity present, that is, the amount of acid or alkali in the crystals would be excessively small.

The influence of a solvent is clearly to give an equilibrium mixture. In the general case of two isomerides forming a solid solution, the stable form is, of course, one particular solid solution of a composition independent of the liquid present. The results show that the freezing point of the equilibrium mixture obtained from various solvents is as follows:

Solvent.	Freezing point of equilibrium mixture.
Light petroleum	82·5°
Ether	82·8
Water	81·0
Alcohol (highest)	78·0

The results in alcohol are untrustworthy for reasons explained above. The differences observed may be due to experimental error —traces of acid, etc.—or they may be due to adsorption of the solvent producing a similar, although smaller, effect to that of acid or alkali. The composition indicated by a freezing point of 82·5° is 75 per cent. of α and 25 per cent. of β. In this connexion it is interesting to note that Fischer described three forms of the substance in question. His third variety, melting about 80°, corresponds with this equilibrium mixture.

It seems probable that the isomerism is stereochemical. Lockemann and Liesche have pointed out that isomerism is very common in hydrazones of the type $\begin{array}{c}A—C—B\\ \|\\ N\cdot NH\cdot C_6H_5\end{array}$, but not in those of the type $\begin{array}{c}A—C—A\\ \|\\ N\cdot NH\cdot C_6H_5\end{array}$, where stereoisomerism is excluded. The structural isomeride, benzeneazoethane, $CH_3\cdot CH_2\cdot N{:}N\cdot C_6H_5$, has been prepared by E. Fischer, and is a red oil.

Several closely allied compounds were investigated in the same way. Acetaldehyde-*p*-bromo- and -*p*-nitro-phenylhydrazones were not found to exhibit isomerism when tested by the above methods, but a similar, although less defined, behaviour was found in the case of acetaldehyde-*p*-tolylhydrazone.

DAUBENY LABORATORY,
MAGDALEN COLLEGE, OXFORD.

CCXXXVIII.—*Theory of Dyeing: the Colour and Molecular State of Picric Acid.*

By William Porter Dreaper, F.I.C.

Picric acid in the anhydrous state is probably colourless. It is nearly so under conditions of long exposure to the action of dehydrating agents acting through a vacuum.

In the colourless condition it has been regarded as having an *o*- or *p*-quinonoid constitution.

An investigation into variations in the conditions of formation of the colourless variety in the presence of fibre colloids (Dreaper and Stokes, *J. Soc. Dyers*, 1909, **25**, 10) with the results now recorded has led to this consideration of the possible molecular structure in relation to its behaviour under these conditions. It may be mentioned that Vignon (*Rev. Gen. Mat. Col.*, 1909, **13**, 156) has compared the dyeing properties of picric acid with the electrical conductivity of its solutions, and that Dreaper and Davis (*Internat. Congr. Appl. Chem.*, 1909, Sect. IV*b*, 7) have confirmed that picric acid in aqueous solution is not subject to de-solution when passing through a sand column. Walker and Appleyard (Trans., 1896, **69**, 1334) have also discussed the dyeing action of picric acid on silk, and have shown that the law of the distribution of picric acid at 60° is:

$$s/\sqrt[2\cdot7]{w} = 35\cdot5.$$

It has been assumed for the purpose in hand that the condition of attraction or strain exhibited by atoms for one another, and the attraction observed as between molecule and molecule, is identical, and in both cases can be referred back to the attraction of atoms acting at varying distances; thus, molecular attraction is regarded as primarily due to the attraction of the atoms in one molecule for those in the surrounding molecules within the active sphere of influence, and not to the attraction of molecule for molecule (see *Chem. News*, 1905, **92**, 299; *Proc. Faraday Soc.*, 1910, 31). It is further assumed that the sum of the primary attraction (as between atom and atom in the same molecule) and the secondary attraction (as between an atom in one molecule and those in others) is at its maximum a constant. The secondary attraction under these conditions would increase as the primary attraction decreases.

It is assumed for the moment that the picric acid molecule is actually in association with x molecules of water (dihydrone or hydronol) in the coloured type. It is difficult to escape this conclu-

sion if this is the cause of a change in molecular structure, and the following facts must then be considered.

The colour intensity apparently increases to a maximum before actual solution takes place, and the ratio of the assembled molecules of water to those of picric acid has increased to a degree where such a change in physical state is involved. Change of colour is therefore not connected in this case with actual solution, unless it is assumed that the one type of picric acid is in solution in the other.

Assuming, therefore, that an association of the order suggested exists, and that this is as between atom and atom, although apparently expressed by outward molecular attraction, and, further, that this attraction under certain conditions may be localised, it will then involve either the H·, NO_2·, OH·, or O groups. Any secondary association may then be represented as follows:

$$-H\,..\,OH_2,\ -NO_2\,..\,OH_2\cdot,\ -OH\,..\,OH_2\cdot,\ \text{or}\ -O\,..\,OH_2\cdot,$$

It will be observed that the last combination is the only one known to exist in the free state. It is suggested that this possible condition correspondingly induces secondary attraction of a localised order, which may then take place as between such units. The assumption that the sum of the primary and secondary attractions has a maximum value has in this respect a definite significance. The effect of such localisation will be to reduce the general attraction (as between molecule and molecule), the former taking its place. If ordinary attraction as between atom and atom be represented by . localised attraction may be written as . . and general attraction as influencing molecule and molecule as . . .

It is seen that association of this localised order is only possible with the quinone or an equivalent type. An equilibrium condition between the picric acid and water molecules may be set up, under which there is a tendency for the colourless type to be replaced by the coloured one.

It is then assumed that the secondary attraction as between the $(OH_2)_x$ molecules and the oxygen atom is sufficient to displace the equilibrium existing between the two types in the direction indicated, and to suppress the ordinary type in favour of the coloured one. The above attraction between the $(OH_2)_x$ molecules and the oxygen atom would under these conditions partly replace that of the ·H atom, and the latter would under these conditions of strain migrate to the neighbouring NO_2-group, with the formation of a compound of quinonoid type.

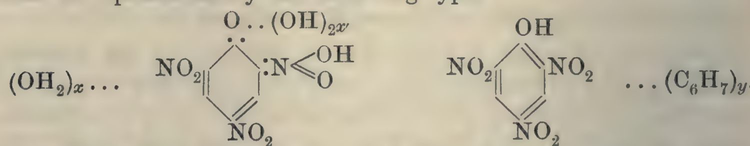
If this localised affinity exists, the oxygen atom, from its isolated position and the fact that it is in combination with a monatomic hydrogen atom, might favour such an action. Be this as it may,

the above consideration affords a possible explanation of the cause of the action observed if the quinone type is actually formed, and if this action is accepted as the cause of the colour change.

The solvent action of toluene when it replaces water is of a different order. In this case the colourless type is present to the virtual exclusion of the coloured one. The yellow variety dissolves to a colourless solution. It must be assumed in this case that association is of a more general order, and non-localised. There is no side-group which can associate with the solvent molecules in the manner suggested in the case of water.

By mass action the water associated with the picric acid in solution is replaced by toluene, and the colourless type is once more in stable equilibrium with the solvent.

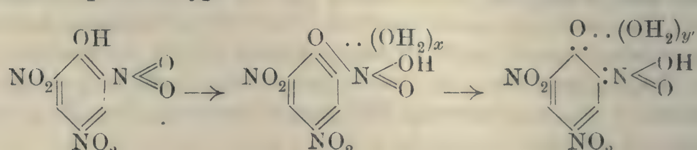
Solutions of picric acid in water and toluene respectively may then be represented by the following types:



In the former case water is represented as being associated locally (. .) as well as generally (. . .). The secondary association may naturally be modified by certain internal groupings, possible close-packing of the atoms, etc., with their attendant condition of strain.

It must be considered whether there is not a more convenient method of considering the change which takes place from one type to the other. If the hydrogen atom migrates, it may well carry with it its bond of attraction, and the change may then be indicated in the following manner. As the mechanism of change in intramolecular condition is apparently in this case a simple one, the change may not necessarily entail the production of the quinone type to allow of salt formation, etc.

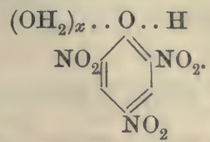
The colour may have its origin in a change of type as indicated below in the intermediate type, which, if unstable, may then pass into the quinone type:



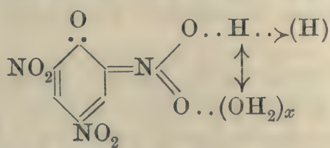
x may or may not equal y in this case.

Alternate methods of association may suggest themselves for comparison with the above. In the quinone type, association may be as between the side-groups generally and the water molecules,

owing to position, but this does not seem to be the case in a solution in toluene; or association may take place as between the $(OH_2)_x$ . . group and the other oxygen atom, as follows:

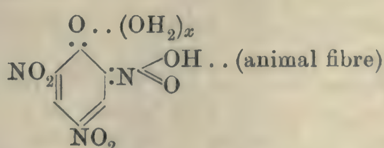


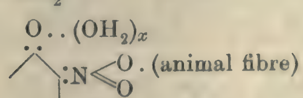
It will be remembered that the loss of colour has also been ascribed to the suppression of free hydrogen ions. In that case of association the presence of free or migrating ions is not impossible, owing to the reduction in the primary bond and an interchange of atoms from one molecule to the other under this condition. This action might be represented graphically in the following manner:

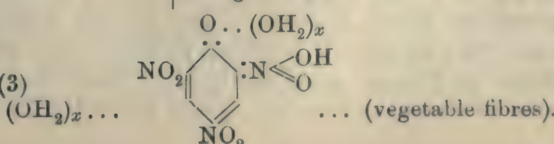


Association may therefore be of a general order, except where conditions are present which supply a tendency to form separate groups or independent units, and then association may be localised in the manner suggested. In the latter case the modification in the general state of equilibrium may be sufficient to disturb the general system and induce certain changes, as in the case of water and picric acid.

The salts of picric acid are coloured, and may be regarded as being of the quinone type. The association as between picric acid and animal and vegetable fibre respectively, where in the former case the change from the coloured type to the colourless does not take place in a vacuum, may possibly be expressed in the following terms:

(1) 

or even (2) 

and (3) 

The colour change can take place in (3), but not in (2), and in the case of silk dyed at 15°, where a certain loss of colour is observed in a vacuum, the change observed may take place in (1), which may be present at such low temperatures of dyeing. This agrees with the experimental results.

EXPERIMENTAL.

The rate of change from the coloured to the colourless type of picric acid when present on the fibres under the action of certain dehydrating agents acting in a vacuum has thus been shown to be of a definite order (Dreaper and Stokes). On vegetable fibres the change is facilitated, whilst on animal fibres it is entirely prevented.

The comparative action of water and toluene on picric acid present within the fibre area has now been examined, it being known that picric acid dissolves in toluene, giving an almost colourless solution.

Silk (fibroïn) was dyed at 95° in the usual manner from an aqueous solution containing 3 per cent. of picric acid of the weight of silk taken, the ratio of silk to solution being 1:200. On immersion in toluene no change in colour or any appreciable re-solution of the dyestuff in the solvent could be observed. This result agrees with that previously obtained with the silk fibre substance and picric acid in a vacuum where this inter-relation prevents any change in type taking place under conditions on which picric acid itself loses colour. As the yellow variety of picric acid passes immediately into a colourless state on solution in toluene, the union between the picric acid and silk fibre-substance evidently prevents this normal change to the colourless type.

When cotton replaces silk, the results are of a different order from those obtained with dehydrating agents. When this fibre is coloured or stained with picric acid from a saturated aqueous solution of the latter, the picric acid is held so loosely that resolution in water is immediate, the colour being removed on agitation with water (ratio of fibre to water=1:1000) in twenty seconds. On the other hand, practically no loss occurred from the fibre area after thirty minutes' extraction with toluene at 17°, nor could any material change from the coloured to the colourless type be observed. The yellow variety is therefore stable (and insoluble) under the conditions indicated.

Following this result, it was observed that cotton may under certain conditions absorb picric acid and dye the fibre an intense yellow shade from its colourless toluene solution. This action seems to depend on the presence of oxycellulose. Under these conditions silk remains colourless, so that the dyeing properties of picric acid

in toluene as judged by colour indications are the reverse of those exhibited in aqueous solution, where the yellow variety is present within the silk area, and the cotton, except in a solution of high concentration, remains white, and absorbs no picric acid.

The silk remained colourless on evaporating the toluene, and the cotton still exhibited a full and brilliant shade of yellow. Samples treated in this manner were subjected to the action of water vapour at 100° and 15° respectively. The silk gradually assumed a yellow shade, and the cotton also visibly deepened in shade; but in water under the conditions before mentioned, the cotton still lost all its colour in twenty seconds; the silk lost about 60 per cent.

A development in shade was noticed on exposure to a damp atmosphere in the place of steam, but the rate of change from the colourless to the coloured type within the fibre area was not so rapid or so complete as after the action of the dehydrating agents, as previously recorded.

The influence of the presence of moisture in the cotton on the result obtained was next investigated. A sample was dried at 110° for one hour, and another was treated with steam before immersion in a solution of picric acid in toluene. The dried sample was much lighter in shade, and the steamed one darker. Taking the depth of shade of the ordinary cotton after treatment as 100, the dried one was represented by 70 and the steamed one by 150. After forty-eight hours' exposure of the samples so treated to the action of a saturated atmosphere at 15°, all the samples developed in colour to a standard shade, indicating that the depth of colour assumed by the fibre at the time of contact is no guide to the amount of picric acid actually absorbed, but only of the proportion of the moisture present in the cotton fibre area.

Cotton containing 6—8 per cent. of natural moisture developed a yellow shade under these conditions, whilst silk containing 10—12 per cent. of natural moisture remained colourless. The nature of the condition under which the water is present within the cotton and silk fibre area is therefore a determining factor. It is possible that in the case of silk the toluene may not penetrate into the silk substance, and therefore no absorption of picric acid can take place; but this does not agree with some of the results obtained. It may be noted that the former assumption has been held to explain certain obscure reactions which occur in the practical manipulation of these fibres.

A sample of silk was immersed in water, and all superfluous moisture carefully removed under pressure in a dry cloth. On subsequent immersion in the toluene solution the silk at once assumed a fairly deep shade of yellow, indicating that the yellow

variety can exist under these conditions in the silk fibre. The action was a non-reversible one, for after drying to remove interfering moisture the colour remained to its full intensity on subsequent immersion in toluene. When once the conditions in the animal fibre are present which determine the formation of the yellow variety, it is apparently more stable than the colourless one.

Sisley has noticed that in dilute solution the whole of the picric acid is present in the water in a mixture of water and toluene, and even in strong solution the ratio is still 4 : 1. The subsequent development of colour in the above samples containing varying amounts of moisture to a common shade does not indicate that the actual adsorption is directly caused by the presence of moisture. This condition seems to govern the ratio of change from the colourless type to the coloured one.

In the case of silk the natural resistance against change is probably due to the fact that the moisture present is in some closer relationship with the fibre colloid, and that this prevents it from reacting with, and producing the colour change with, picric acid observed in the case of cotton; but this change can take place in the presence of water, which is not so closely associated with the fibroin. When the change has taken place as in the case of a silk fibre which obviously contained "free" moisture, some further action between the silk substance and the yellow type prevents the subsequent reversion to the colourless type in the presence of toluene.

Thus, whilst "free" moisture must be present in order that the yellow variety may exist in the silk fibre area, yet there is an adsorption of the colourless variety from toluene in its absence. This follows from the fact that on subsequent steaming the colourless silk develops a yellow shade, even after a final treatment with toluene to remove any surface picric acid which in itself might account for this action.

The relationship which exists between an animal fibre-substance and picric acid which prevents or inhibits the loss of colour on exposure to the dehydrating agents, and resists resolution and a return to the colourless type in the presence of toluene, is apparently different in the case of vegetable fibres. The action of dehydrating agents in this case causes the cotton to lose its colour, but does not do this in the presence of toluene, so that these reactions indicate in further detail the nature of the affinity which apparently exists between the fibre and the picric acid.

It may be argued that an affinity exists between the picric acid and cotton fibre-substance which prevents the normal change to the colourless type taking place in the presence of toluene; so that

whilst the picric acid is easily removed by water from the fibre area, this action cannot take place in the case of toluene. This agrees with the assumption that the yellow variety is insoluble as such in toluene, and that the latter cannot bring about a change of type in the presence of the cotton fibre-substance. The yellow variety being soluble in water is easily removed. As picric acid will dye cotton from a toluene solution, it may be argued that this suppression of colour change is not due to any want of penetration of the solvent into the fibre.

The results obtained may be summarised in the following manner:

Nature of Fibre.	Action of dehydrating agents acting through a vacuum.	Action of toluene on picric acid within the fibre area.
Silk	No loss in colour	No loss in colour
Wool	,, ,,	,, ,,
Cotton	Loss of colour in excess of that in acid itself	,, ,,

CCXXXIX.—*Formation of Six- and Seven-membered Rings from Derivatives of* 2 : 2′-*Ditolyl.*

By James Kenner and Emily Gertrude Turner.

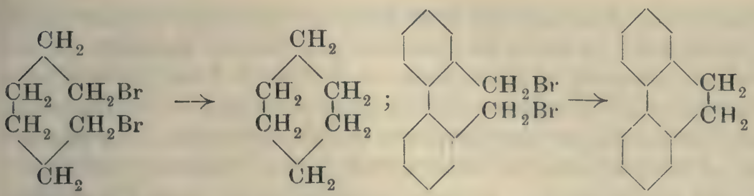
The general problem of the formation of closed rings from open-chain compounds has been the subject of repeated investigation, and in their broad outlines the results may be said to be capable of interpretation in terms of Baeyer's strain theory. Whilst, however, the stability, and therefore presumably the readiness of formation, of any ring is largely determined by the number of carbon atoms composing it, the relative position and nature of the substituent groups also play an important part. Although comparatively little attention has been bestowed on this side of the subject, it is possible to say: "dass im allgemeinen das Vorkommen eines quaternär gebundenen Kohlenstoffatoms die Aufspaltbarkeit zu erhöhen scheint" (Aschan, "Chemie der alicyclischen Verbindungen," 1905, p. 244), and, further, that the rupture of the ring takes place at the point where this atom occurs. It seems not impossible that the various groups attached to the carbon atom have an effect on each other similar in nature to that which is assumed to give

rise to the phenomena of steric hindrance and inhibition, or, in other words, that a more extended application of Baeyer's theory is required. From this point of view it is to be expected that the ease with which cyclic condensation occurs will be modified by the presence in the chain of some carbon atoms which, being already members of a closed ring, have the directions of their valencies to some extent determined. The extent of this modification, should it occur, will necessarily be determined by the number of the carbon atoms of this type involved in the production of the new ring and by the degree of strain to which those of their valencies already engaged were subjected.

At the present time the compounds most easily obtainable for the study of this type of cyclic condensation are those in which certain of the carbon atoms form part of six-membered rings; thus *o*-xylene and its derivatives, the *peri*-derivatives of naphthalene, and 2:2′-derivatives of diphenyl respectively contain two, three, and four such atoms. The possibility of forming rings from xylene and naphthalene has been investigated frequently, but as a result of the difficulty which formerly doubtless attended their preparation, diphenyl derivatives have received little attention. Ullmann's discovery that 2:2′-ditolyl is readily obtained by the action of copper powder on *o*-iodotoluene (*Annalen*, 1904, **332**, 28) has removed the difficulty in this case, and, as the method proved to be suitable for the preparation of the compound in quantity, we were encouraged to undertake a systematic investigation of the formation of closed rings from it.

In the first place, $\omega\omega'$-dibromo- and $\omega\omega\omega'\omega'$-tetrabromo-2:2′-ditolyl were prepared. It was found that 2:2′-ditolyl reacted vigorously with bromine at 110°, and the dibromo-derivative was readily isolated. The further bromination was considerably more difficult, and only those preparations of the tetrabromo-derivative were successful in which the addition of the bromine extended over a period of at least two days.

The action of sodium on polymethylene dibromides is well known as a fruitful method for the synthesis of closed-ring compounds, and was shown by Haworth and Perkin (Trans., 1894, **64**, 599) to give excellent results when applied to hexamethylene dibromide, of which $\omega\omega'$-dibromo-2:2′-ditolyl is a derivative. In the case of the latter substance, it was found that its ethereal solution readily reacted with sodium when the mixture was heated. The reaction to some extent followed a course similar to that observed for hexamethylene dibromide:



for the presence of dihydrophenanthrene in the product was readily shown by its oxidation to phenanthraquinone. The yield of phenanthrene derivative was not as favourable as that of *cyclo*-hexane, for there was also produced a colourless hydrocarbon, evidently of high molecular weight, the nature of which has not yet been determined.

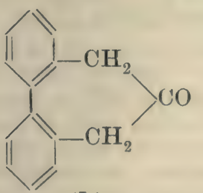
Apart from the formation of the six-membered ring in this case, this reaction has the further interest that ωω′-dibromo-2:2′-ditolyl is a possible intermediate product * in the production of dihydrophenanthrene from *o*-bromobenzyl bromide, described by Jackson and White (*Amer. Chem. J.*, 1881, **2**, 383).

By the action of sodium on ωωω′ω′-tetrabromo-2:2′-ditolyl, phenanthrene itself was obtained in good yield:

$$\begin{array}{l} C_6H_4\cdot CHBr_2 \\ | \\ C_6H_4\cdot CHBr_2 \end{array} + 4Na \longrightarrow \begin{array}{l} C_6H_4\cdot CH \\ | \qquad \| \\ C_6H_4\cdot CH \end{array} + 4NaBr.$$

It may be remarked that this synthesis of phenanthrene is the first in which the hydrocarbon has been obtained by a series of reactions, all of which may be carried out at comparatively low temperatures.

Attention was then directed to the isolation of compounds containing the hitherto unknown combination of a seven-membered ring with two six-membered rings. For this purpose the preparation of the ketone (I) was attempted, as the researches of Baeyer and others have shown that such cyclic ketones constitute one of the most convenient starting points for synthetical operations of this kind:



(I.)

Whilst the method involving the dry distillation of the salts of

* Experiments are in progress having for their object the preparation of another possible intermediate product, 2:2′-dibromodibenzyl, in order that the behaviour of this compound may be studied.

dibasic acids is perhaps the most generally applicable in such cases, it necessitates the use of considerable quantities of material. Moreover, the isolation of the heptanone derivative from the distillate might probably be difficult without some knowledge of its properties. This information we have sought to gain by attempting the production of the compound by other means before proceeding to investigate the conditions most suitable for its formation from 2:2′-ditolyl-ωω′-dicarboxylic acid.

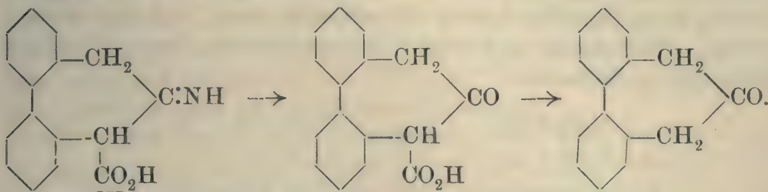
2:2′-Ditolyl-ωω′-dicarboxylonitrile had been chosen as a source of this acid, and was prepared from ωω′-dibromo-2:2′-ditolyl in the manner described for *o*-phenylenediacetonitrile by Moore and Thorpe (Trans., 1908, **93**, 165). It was then found that this compound could be made to undergo condensation by the method applied to *o*-phenylenediacetonitrile by these authors, and we turned our attention to this condensation as likely to provide an easier means of preparing the ketone than that originally contemplated. The condensation, effected under the influence of sodium ethoxide, leads to the production of 1-*imino*-2-*cyano*-3:5-*dibenzo*-$\Delta^{3:5}$-cyclo*heptadiene* * (II):

(II.)

This iminocyano-compound shows considerable stability, and is only very slowly decomposed by hot aqueous potassium hydroxide. Its behaviour towards cold concentrated sulphuric acid corresponds with that of β-imino-α-cyanohydrindene, and leads to the formation

* The system of nomenclature proposed for these compounds is based on that which has been adopted in the case of compounds in which one benzene ring is combined with a seven-membered ring. The only compounds of this type described in the Transactions (Kipping and Hunter, Trans., 1901, **79**, 602) are termed pheno*cyclo*heptane derivatives. The prefix "pheno-" seems, however, to have been generally discarded in favour of "benzo-" (compare Thiele and Schneider, *Annalen*, 1909, **369**, 288; Thiele and Weitz, *ibid.*, 1910, **377**, 1; papers by Scholl, in the *Berichte*, on benzanthrone derivatives, and Aschan, "Chemie der alicyclischen Verbindungen," 1905, p. 886). Further, as the proposed generic name emphasises the derivation of these compounds from *cyclo*heptane, any system of numbering should commence from an atom of the seven-membered ring. The choice of the particular atom is conveniently regulated by the ordinary rules of the Geneva nomenclature. The position of the "benzo-" nuclei in the heptamethylene ring is denoted according to the same plan as that in general use for double linkings. In the case of compounds containing substituents in the six-membered rings, the numbering could be continued in these rings, commencing with the carbon atom adjacent to that one

of 1-*imino*-3 : 5-*dibenzo*-$\Delta^{3:5}$-cyclo*heptadiene*-2-*carboxylic acid* (III). By the action of hot dilute sulphuric acid on this compound, the desired ketone, 3 : 5-*dibenzo*-$\Delta^{3:5}$-cyclo*heptadien*-1-*one*, was obtained. This reaction can be explained by assuming that the imino-compound is hydrolysed in the first place to the corresponding keto-compound, and this, as an α-ketonic acid, is decomposed by the dilute acid, with the loss of carbon dioxide:

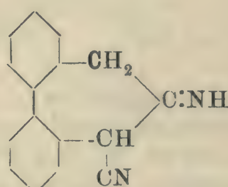


(III.)

These imino-compounds were not examined more closely than was necessary for the immediate purpose in view, but it was observed that they do not show the colour reactions with oxidising agents which are characteristic of the hydrindene derivatives described by Moore and Thorpe. These authors showed that the colour in the case of β-imino-α-cyanohydrindene is due to the formation of bis-1-cyano-2-hydroxyindene (IV):

$$\mathrm{CN{\cdot}C}{<}\begin{matrix}\mathrm{C(OH)}\\ \mathrm{C_6H_4}\end{matrix}{>}\mathrm{C{:}C}{<}\begin{matrix}\mathrm{C(OH)}\\ \mathrm{-C_6H_4-}\end{matrix}{>}\mathrm{C{\cdot}CN}$$

(IV.)



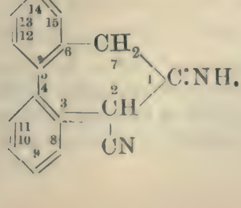
(V.)

It is not improbable that the failure of the reaction in the case of 1-imino-2-cyano-3 : 5-dibenzo-$\Delta^{3:5}$-*cyclo*heptadiene (V) is due to steric causes, as it is unlikely that the carbon atom **C** can come within the sphere of action of a similar carbon atom in a second molecule of the compound.

The readiness with which phenanthrene was formed from

of the four common to two rings which takes precedence in the numbering of the *cyclo*heptane ring.

This system of numbering is shown in the diagram for the imino-compound referred to above:



ωωω′ω′-tetrabromo-2 : 2′-ditolyl made the study of condensations with the corresponding dialdehyde a matter of interest. This dialdehydodiphenyl * was readily obtained from ωωω′ω′-tetrabromo-2 : 2′-ditolyl by hydrolysis with potassium oxalate in dilute alcoholic solution. When submitted to the action of concentrated potassium hydroxide solution, on the lines of the Cannizzaro reaction, a hydroxy-acid (with its lactone) was obtained. The acid proved to be *ω-hydroxy-2-methyldiphenyl-2′-carboxylic acid*, and the analogy between this reaction and that which occurs with benzaldehyde is shown by the formulæ:

$$\begin{array}{lcl} C_6H_5\cdot CHO & & C_6H_5\cdot CH_2\cdot OH \\ & \longrightarrow & \quad + \qquad ; \\ C_6H_5\cdot CHO & & C_6H_5\cdot CO_2H \end{array}$$

$$\begin{array}{lcl} C_6H_4\cdot CHO & & C_6H_4\cdot CH_2\cdot OH \\ | & \longrightarrow & | \qquad\qquad . \\ C_6H_4\cdot CHO & & C_6H_4\cdot CO_2H \end{array}$$

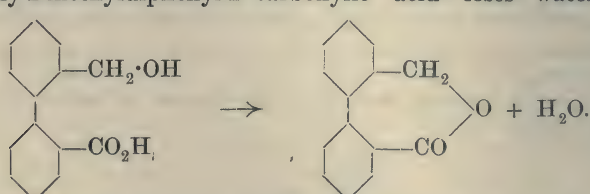
The reaction is of great interest in view of the experimental evidence adduced by Claisen (*Ber.*, 1887, **20**, 646) and by Kohn and Trantom (Trans., 1899, **75**, 1155) in support of the hypothesis that a compound (A) is formed as an intermediate product from benzaldehyde:

$$\left.\begin{array}{l} C_6H_5\cdot C(OH)(OK) \\ C_6H_5\text{———}CH_2 \end{array}\right\rangle O \qquad\qquad \left.\begin{array}{l} C_6H_4\cdot C(OH)(OK) \\ | \\ C_6H_4\text{———}CH_2 \end{array}\right\rangle O$$

A. B.

The application of this conception to the condensation of 2 : 2′-dialdehydodiphenyl would involve either the formation of the substance (B) or a series of similar reactions in which two separate molecules condense, as illustrated by the reaction encountered in the case of terephthalaldehyde, which leads to the formation of ωω′-dihydroxy-*p*-xylene, terephthalic acid, and ω-hydroxy-*p*-toluic acid (Grimaux, "Jahresbericht über die Fortschritte der Chemie," 1876, 490).

Actually it would seem that (B) is the intermediate product, for ω-hydroxy-2-methyldiphenyl-2′-carboxylic acid loses water when



* Since this paper was written, F. Meyer has published (*Ber.*, 1911, **44**, 2305) an account of the preparation of this compound from *o*-iodobenzaldehyde. The aldehyde was not obtained by him in the solid condition, but was characterised by the preparations of certain derivatives. The compound was first described by us (Proc., 1911, **27**, 92).

heated to 110°, forming an ε-lactone, which stands in close relationship to (B). By hydrolysis this lactone is reconverted into the hydroxy-acid.

The formation of an ε-lactone is so unusual that it is of interest to note that, so far as we are aware, only one other case has been recorded in which an ε-lactone is formed directly from the hydroxy-acid by loss of water. Baeyer and Seuffert (*Ber.*, 1899, **32**, 3619) found that βζ-dimethyloctan-ε-oloic acid readily forms a lactone, whilst Baeyer and Villiger prepared this and another ε-lactone, and even a ζ-lactone, by the action of Caro's acid on menthone, tetrahydrocarvone, and suberone respectively.

The behaviour of 2:2′-dialdehydodiphenyl just described also agrees with that of the *o*-xylene derivative, for Thiele and Günther (*Annalen*, 1906, **347**, 107) mention that *o*-phthalaldehyde yields phthalide by interaction with potassium hydroxide. Further, it is well known that diphenic acid, like phthalic acid, readily yields an anhydride on dehydration with acetyl chloride, whereas adipic acid, of which diphenic acid is a substitution derivative, under the same conditions only furnishes a small amount of anhydride, even after prolonged treatment (Étaix, *Ann. Chim. Phys.*, 1896, [vii], **19**, 356); also an imide of diphenic acid, but not of adipic acid, is known. The unusual ease with which seven-membered rings are formed in these cases supports the view that the 2:2′-position in diphenyl derivatives is frequently an effective ortho-position.* In this connexion Täuber's observation that 2:2′-diaminodiphenyl condenses with benzil in the same manner as *o*-diamines (*Ber.*, 1892, **25**, 3287; 1893, **26**, 1703) is not without interest.

If it be assumed that two double bonds are present in the 3:4- and 5:6-positions rather than in the 3:8- and 5:15-positions of the dibenzo*cyclo*heptadiene molecule, and that these double bonds have the usual stability associated with their presence in benzene rings, it may be pointed out that the strain, in Baeyer's sense of the word, is not nearly so large as is usually attributed to the *cyclo*-heptane ring; for the angle between any single bond and the plane of two others is 125°16′. The *cyclo*heptadiene ring involved in the present case contains four such angles, together with three of 109°28′, amounting in all to 829°18′. The deficiency or total strain is therefore 70°32′, as contrasted with 133°44′ in the case of the saturated ring, and the average deviation of each of the fourteen valencies (the two valencies of each double bond being considered

* Experiments are contemplated with the object of determining to what extent this resemblance holds, for it may be expected that limitations will exist just as they are known to occur in the case of the relationship between the *peri*-position of naphthalene and the ortho-position.

to act together in such a case) becomes 5°2′, or rather less than the mean deviation in the *cyclo*hexane ring. A similar calculation in the case of benzene itself reveals an average strain of 2°38′. In general, the presence of such double bonds would tend to diminish the strain of rings containing six or more carbon atoms, and to increase it in the case of rings containing less than six carbon atoms.

The benzoin reaction was also applied to 2:2′-dialdehydodiphenyl in the hope that intramolecular condensation might also take place in this case, leading to the formation of 9:10-dihydroxyphenanthrene:

$$\begin{array}{l} C_6H_4\cdot CHO \\ | \\ C_6H_4\cdot CHO \end{array} \longrightarrow \begin{array}{l} C_6H_4\cdot CH\cdot OH \\ | \qquad\quad | \\ C_6H_4\cdot CO \end{array} \rightleftarrows \begin{array}{l} C_6H_4\cdot C\cdot OH \\ | \qquad\quad \| \\ C_6H_4\cdot C\cdot OH \end{array}.$$

Actually, however, it would seem that two separate molecules of dialdehydodiphenyl are concerned, for, although the amorphous product of the reaction was too ill-defined to allow of its isolation in the pure condition, it showed the reactions of a benzoin. It had reducing properties, and on oxidation was converted into an *o*-diketone, which, however, was not phenanthraquinone.

Experimental.

The 2:2′-ditolyl used in the following experiments was prepared according to the method described by Ullmann (*loc. cit.*) by heating equal weights of *o*-iodotoluene and copper bronze ("Naturkupfer C") under pressure at 230°. At higher temperatures the yields were not quite so good, but in all cases products of much higher boiling point accompanied the 2:2′-ditolyl.

ωω′-Dibromo-2:2′-ditolyl.

The bromination was carried out in a reflux apparatus so arranged that the bromine was introduced below the surface of the ditolyl. There was a distinct evolution of gas at 90°, but the mixture was heated at 110° in order to accelerate the reaction, which, it may be mentioned, took place more rapidly in sunlight than in the dark. After the calculated quantity of bromine had been added, the heating was continued until the evolution of gas had ceased and the dark red liquid was transparent, the temperature being raised if necessary to 120°. Neglect of this precaution in one case caused a considerable diminution in the yield. The product was kept in a vacuum desiccator over potassium hydroxide for some days while the dibromo-compound crystallised out. After adhering oil * had been separated as completely as possible, the solid was

* An attempt to utilise this oil for the preparation of the tetrabromo-derivative (p. 2112) was unsuccessful.

crystallised from acetone, being obtained in large, rhombic prisms, melting at 87·5°. The weight of pure product thus obtained amounted to two-thirds of the weight of ditolyl used:

0·1379 gave 0·2507 CO_2 and 0·0442 H_2O. C=49·57; H=3·56.
0·1868 „ 0·2083 AgBr. Br=47·44.
$C_{14}H_{12}Br_2$ requires C=49·41; H=3·56; Br=47·02 per cent.

Action of Sodium on ωω′-Dibromo-2:2′-ditolyl.

The dibromo-derivative dissolved in dry ether was gently boiled with successive quantities of sodium powder until the metal was no longer attacked. After decantation and removal of the ether, a mobile oil was obtained, from which after some days a minute quantity of unchanged dibromide separated. Beyond this, no separation could be obtained, an unexpected result, as dihydrophenanthrene melts at 94—95° (Schmidt and Mezger, *Ber.*, 1907, **40**, 4248). To discover if this substance had been produced, a portion of the oil was treated with picric acid solution in the manner described by these authors, and the characteristic colour change from yellow to red was observed, although attempts to separate the red picrate from the excess of picric acid were unsuccessful. Eventually the yield of dihydrophenanthrene was estimated by oxidising the oil with a solution of chromic acid in glacial acetic acid, and found to be 26 per cent. The phenanthraquinone after purification melted at 205°, answered all the well known reactions, and, further, was identified by analysis. (Found, C=80·56; H=3·99. Calc., C=80·76; H=3·88 per cent.)

During the action of sodium on the ethereal solution just described, the separation of a colourless, amorphous substance was observed. This was soluble in benzene, but resisted all attempts to crystallise it, being obtained as a brittle deposit after evaporation of the solvent, and has not been examined further than to show that it is free from halogen.

2:2′-*Ditolyl-ωω′-dicarboxylonitrile.*

The methods used in the preparation of this compound and of its derivatives were essentially those applied by Moore and Thorpe (*loc. cit.*) in the case of *o*-phenylenediacetonitrile.

A saturated aqueous solution of potassium cyanide (5·2 grams) was mixed with about three times its volume of absolute alcohol. The mixture was heated to the boiling point, and to it finely powdered ωω′-dibromo-2:2′-ditolyl (12 grams) was added in small portions. After remaining at 50—60° for some hours, water was added to the product, and the nitrile obtained as an oil which

readily solidified, and, after crystallisation from alcohol, formed rectangular blocks, melting at 77°. The yield was about 90 per cent. of the calculated amount:

0·1658 gave 17·15 c.c. N_2 at 15·5° and 747 mm. N=12·04.
$C_{16}H_{12}N_2$ requires N=12·09 per cent.

2:2′-*Ditolyl*-ωω′-*dicarboxyamide.*

This compound was prepared by allowing the solution of the nitrile in five times its weight of concentrated sulphuric acid to remain overnight. On pouring the mixture into water and rendering the solution alkaline with ammonia, a quantity of the amide was precipitated, the weight of which was rather less than that of the nitrile used. This compound is only sparingly soluble in benzene, chloroform, or light petroleum, but dissolves readily in alcohol, from which it separates in clusters of fine needles, melting at 210—211°:

0·1452 gave 0·3800 CO_2 and 0·0810 H_2O. C=71·37; H=6·19.
0·1280 ,, 12·1 c.c. N_2 at 25° and 752 mm. N=10·67.
$C_{16}H_{16}O_2N_2$ requires C=71·64; H=5·97; N=10·45 per cent.

2:2′-*Ditolyl*-ωω′-*dicarboxylic Acid.*

The hydrolysis of the amide just described was effected by boiling it with 10 per cent. potassium hydroxide solution until the evolution of ammonia, which was only slow, had ceased. After acidification, the product was repeatedly extracted with ether, and, after removal of the ether, crystallised from water. 2:2′-*Ditolyl*-ωω′-*dicarboxylic acid* crystallises in prisms, melting at 152°:

0·1438 gave 0·3750 CO_2 and 0·0698 H_2O. C=71·17; H=5·23.
$C_{16}H_{14}O_4$ requires C=71·12; H=5·22 per cent.

1-*Imino*-2-*cyano*-3:5-*dibenzo*-$\Delta^{3:5}$-cyclo*heptadiene.*

To prepare the imino-compound a solution of 2:2′-ditolyl-ωω′-dicarboxylonitrile in four times its weight of absolute alcohol was boiled with a small amount of sodium ethoxide for one hour in a current of hydrogen. After about half an hour the imino-compound began to separate from the hot solution in colourless, prismatic crystals, and the yield amounted to over 80 per cent. of that calculated. The product melted at 189°:

0·1179 gave 0·3562 CO_2 and 0·0586 H_2O. C=82·4; H=5·53.
0·1336 ,, 0·4034 CO_2 ,, 0·0634 H_2O. C=82·25; H=5·27.
0·1988 ,, 20·4 c.c. N_2 at 23° and 754 mm. N=11·72.
$C_{16}H_{12}N_2$ requires C=82·76; H=5·17; N=12·07 per cent.

As this compound does not give a colour reaction with concentrated sulphuric acid or with alcoholic potassium hydroxide, it might be expected that no advantage would result from the maintenance of an oxygen-free atmosphere during the preparation, but experience showed that better results were always obtained when hydrogen was used.

Ammonia was evolved only slowly when the imino-compound was boiled with 20 per cent. potassium hydroxide solution, and the decomposition was not complete even after two days.

1-*Imino*-3 : 5-*dibenzo*-$\Delta^{3:5}$-cyclo*heptadiene*-2-*carboxylic Acid*.

A solution of 1-imino-2-cyano-3 : 5-dibenzo-$\Delta^{3:5}$-*cyclo*heptadiene (4 grams) in cold sulphuric acid (40 c.c.) was left overnight, and then poured on to ice. After some time the precipitate was collected and found to be completely soluble in sodium hydroxide solution. The acid was therefore free from amide, and, after reprecipitation, was crystallised from dilute alcohol. It formed colourless needles, melting at 180°:

0·1910 gave 0·5328 CO_2 and 0·0890 H_2O. C=76·08; H=5·18.
0·2172 „ 11·0 c.c. N_2 at 29° and 759 mm. N=5·68.
$C_{16}H_{13}O_2N_2$ requires C=76·49; H=5·18; N=5·58 per cent.

3 : 5-*Dibenzo*-$\Delta^{3:5}$-cyclo*heptadien*-1-*one*.

A mixture of 1-imino-3 : 5-dibenzo-$\Delta^{3:5}$-*cyclo*heptadiene-2-carboxylic acid (3 grams) with 50 per cent. sulphuric acid (100 grams) was boiled in a reflux apparatus until all the solid had disappeared, a change which was complete after about one and a-half hours. By extraction with ether the ketone was isolated, being obtained as an oil, which completely solidified after some time. It separated from alcoholic solution in large, faintly yellow, hexagonal crystals, melting at 78—79°, but if isolated from the acid liquid by distillation with steam it is colourless. The yield was 80 per cent. of that calculated:

0·1054 gave 0·3342 CO_2 and 0·0568 H_2O. C=86·55; H=5·99.
$C_{15}H_{12}O$ requires C=86·54; H=5·77 per cent.

The *oxime* crystallises in needles from dilute alcohol, and melts at 189°. For analysis it was dried at 130°:

0·2688 gave 16·2 c.c. N_2 at 27° and 750·5 mm. N=6·58.
$C_{15}H_{13}ON$ requires N=6·27 per cent.

ωωω′ω′-Tetrabromo-2:2′-ditolyl.

The bromination of 2:2′-ditolyl was carried out in its earlier stages at 110°, the temperature being gradually raised to 140°, and about 10 per cent. more than the calculated quantity of bromine was used. Experiments in which all the bromine was added in the course of one day repeatedly failed to give more than a minute proportion of the tetrabromo-derivative, but by arranging that the addition extended over more than two days a quantity of the tetrabromo-derivative, rather less in weight than the ditolyl used, was obtained. If the bromination had been properly conducted, the dark-coloured oil immediately became very viscous when poured into a dish, but did not crystallise when kept over potassium hydroxide in a desiccator. The mass set solid when it was treated with a little warm light petroleum, and was then crystallised from this solvent. The tetrabromo-derivative resembles the dibromo-derivative in crystalline form, and melts at 138°:

0·1612 gave 0·2015 CO_2 and 0·0302 H_2O. C = 34·10; H = 2·08.
$C_{14}H_{10}Br_4$ requires C = 33·75; H = 2·02 per cent.

Action of Sodium on ωωω′ω′-Tetrabromo-2:2′-ditolyl.

The reaction was carried out in the same manner as in the case of the dibromo-derivative. The ethereal solution from 10 grams of the tetrabromo-derivative gave 2·4 grams of crude phenanthrene (m. p. 98°). By crystallisation from 70 per cent. alcohol, the hydrocarbon was obtained in white leaflets (Found, C = 94·15; H = 6·00. Calc., C = 94·34; H = 5·66 per cent.), from which, for purposes of identification, the picrate (yellow needles, m. p. 143°) was prepared.

2:2′-Dialdehydodiphenyl.

When ωωω′ω′-tetrabromo-2:2′-ditolyl is heated at 130° with sulphuric acid, partial carbonisation instead of the expected hydrolysis takes place, accompanied by evolution of bromine, hydrogen bromide, and sulphur dioxide, a considerable amount of the tetrabromo-derivative being recovered unchanged. Recourse was therefore had to the method of hydrolysis described by Thiele and Günther (*Annalen*, 1906, **347**, 107) for the preparation of *o*-phthalaldehyde from *o*-xylylene tetrabromide. Ten grams of ωωω′ω′-tetrabromo-2:2′-ditolyl were heated in a reflux apparatus on the water-bath with 20 grams of potassium oxalate and 200 c.c. of 50 per cent. alcohol. The substance had dissolved completely after forty hours' boiling, and the pale yellow solution was then

added to twice its volume of water. The aldehyde separated after some hours, the yield amounting to that calculated.

The aldehyde is best purified by adding light petroleum (b. p. 40—60°) to its solution in ether, and is thus obtained in leaflets, colourless when pure, but frequently slightly yellow, and melting at 62°. It can also be crystallised from light petroleum (b. p. 60—80°), but the process of solution is accompanied by the formation of a considerable amount of oily matter:

0·0972 gave 0·2860 CO_2 and 0·0428 H_2O. C=80·25; H=4·89.

$C_{14}H_{10}O_2$ requires C=79·98; H=4·80 per cent.

The *phenylhydrazone* crystallises in rectangular prisms from alcohol, and when exposed to light changes in colour from a light yellow to a bright red:

0·1424 gave 16·2 c.c. N_2 at 26° and 756 mm. N=13·17.
0·1528 „ 16·8 c.c. N_2 „ 26° „ 756 mm. N=12·73.

$C_{26}H_{22}N_4,C_2H_5{\cdot}OH$ requires N=12·88 per cent.

Action of Potassium Hydroxide on 2:2′-Dialdehydodiphenyl.

Two grams of the finely powdered aldehyde were well shaken with a cold solution of 20 grams of potassium hydroxide in 14 c.c. of water until an emulsion had been formed. After twenty-four hours the mixture was diluted and repeatedly extracted with ether in order to remove any colouring matter due to impurity in the aldehyde. The solution was then cooled and acidified. After a short time the precipitate (1·9 grams) was collected, and roughly separated into its components by treatment with ammonia solution.

The undissolved portion, purified by crystallisation from dilute alcohol, was obtained in elongated prisms, melting at 132°. From absolute alcohol it crystallised in diamond-shaped prisms:

0·1270 gave 0·3708 CO_2 and 0·0550 H_2O. C=79·63; H=4·81.
0·0714 „ 0·2080 CO_2 „ 0·0308 H_2O. C=79·45; H=4·7.

$C_{14}H_{10}O_2$ requires C=80·00; H=4·76 per cent.

The portion soluble in ammonia was re-precipitated by acid, and purified by repeated crystallisation from a mixture of ether and light petroleum (b. p. 40—60°), in the latter of which solvents it is sparingly soluble. It separated in small, well-defined, prismatic crystals, which melted at 146°:

0·1348 gave 0·3654 CO_2 and 0·0636 H_2O. C=73·93; H=5·24.

$C_{14}H_{12}O_3$ requires C=73·68; H=5·26 per cent.

The composition of the two substances thus pointed to the existence of a relationship between them of lactone to hydroxy-acid, and their intimate connexion was further illustrated by the conversion of the former substance into the latter through the agency

of potassium hydroxide solution, and by the observation that the acid substance lost the elements of water at 110° and passed into the non-acid product.

In conclusion, the authors desire to express their thanks to Professor Wynne for much encouragement and advice during the course of this work.

THE UNIVERSITY,
SHEFFIELD.

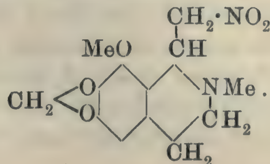
CCXL.—*Synthetical Experiments in the Group of the* iso*Quinoline Alkaloids. Part II. The Constitution of the Condensation Products of Cotarnine and the Condensation of Cotarnine with Aliphatic and Aromatic Nitro-compounds.*

By EDWARD HOPE and ROBERT ROBINSON.

THE peculiar reactivity of cotarnine towards nitro-compounds was first observed in the case of the condensation of this substance with nitromeconine (Hope and Robinson, Proc., 1910, **26**, 228), whereby nitrognoscopine (nitro-*r*-narcotine) resulted, and in Part I. of this investigation an account has been given of a closely related reaction, namely, that resulting in the production of anhydrocotarnine-5-nitrophthalide (this vol., p. 1153). By elimination of the nitro-group this substance was converted into anhydrocotarninephthalide, which may also be called dedimethoxygnoscopine, and the method of synthesis of alkaloids of the *iso*quinoline group which was thus indicated appeared to be worthy of a detailed examination.

The object of the present communication is to place on record the preparation of a number of compounds derived from cotarnine by condensation in the main with nitrotoluenes, and some of these, and also the condensation product with nitromethane, we propose to examine further, especially with a view to their conversion into bases free from nitro-groups allied in constitution to the naturally occurring *iso*quinoline alkaloids.

Cotarnine condenses with particular readiness with nitromethane, and the product is a crystalline base, *anhydrocotarninenitromethane*, to which we ascribe the constitution:



Although there can be no doubt that the substance is homogeneous, two distinct methiodides are obtained by the action of methyl iodide; the one produced in larger amount is probably the normal methiodide, whilst the other, a bright yellow substance, yields trimethylamine on treatment with alkali, a fact which in conjunction with analytical data indicates it as possessing the constitution:

$$CH_2{:}O_2{:}C_6H(OMe){<}\genfrac{}{}{0pt}{}{CH{:}CH{\cdot}NO_2}{CH_2{\cdot}CH_2{\cdot}NMe_3I}\cdot$$

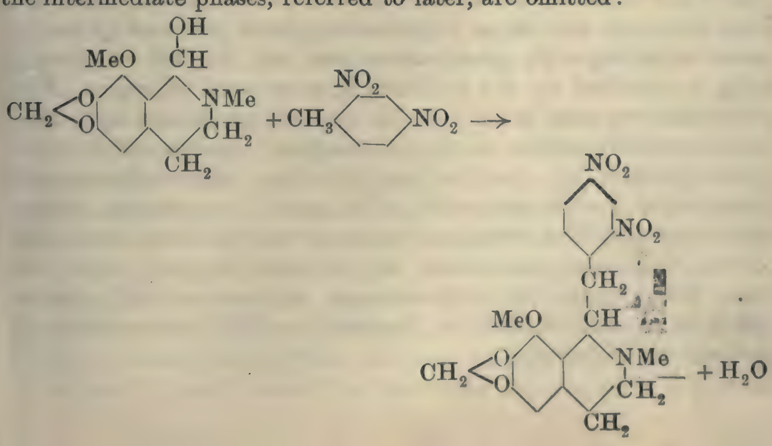
Nitroethane also yields a condensation product with cotarnine, but it has only been isolated in the form of its methiodide, whilst the other nitro-paraffins, such as the two nitropropanes and nitropentane, apparently react with great difficulty.

A series of nitrobenzylhydrocotarnines is produced by the condensation of cotarnine with nitrotoluenes.

The mononitro-compounds are obtained in moderate yield by the condensation of cotarnine with *o*- or *p*-nitrotoluene in the presence of sodium ethoxide in alcoholic solution. They are stable bases not decomposed on boiling with glacial acetic acid.

The dinitro-compounds are produced in almost quantitative yield by boiling an alcoholic solution of cotarnine and dinitrotoluene. 2:4:6-Trinitrotoluene on suspension in a cold alcoholic solution of cotarnine yields the theoretical amount of *anhydrocotarnine-2:4:6-trinitrotoluene*, the reaction being complete in a few seconds. Trinitro-*m*-xylene is less reactive, and cotarnine residues attach to both methyl groups, whilst with trinitromesitylene an even more sluggish reaction is observed, and the product is *dianhydrodicotarninetrinitromesitylene*.

All these condensations occur in accordance with the following scheme, in which the case of 2:4-dinitrotoluene is represented, and the intermediate phases, referred to later, are omitted:



The cyclic constitution assigned to these condensation products is justified in this particular instance by the results obtained in examining the exhaustive methylation of the base.

Anhydrocotarnine-2:4-*dinitrotoluene methiodide* (I) yields, by conversion into the methochloride and treatment with alkali, the *base* (II), which in turn yields a *methiodide*. The *methyl hydroxide* (III) corresponding with this salt possesses considerable stability, but is slowly decomposed on boiling with water, the products being trimethylamine and the neutral substance (IV). The constitution of this final product was proved by its synthesis from cotarnone and 2:4-dinitrotoluene (see p. 2131):

$$CH_2{:}O_2{:}C_6H(OMe){<}\begin{array}{l} C_6H_3(NO_2)_2 \\ | \\ CH_2 \\ | \\ CH-NMe_2I \\ | \\ CH_2\cdot CH_2 \end{array} \quad \text{(I.)} \qquad C_8H_6O_3{<}\begin{array}{l} CH{:}CH\cdot C_6H_3(NO_2)_2 \\ CH_2\cdot CH_2\cdot NMe_2 \end{array} \quad \text{(II.)}$$

$$C_8H_6O_3{<}\begin{array}{l} CH{:}CH\cdot C_6H_3(NO_2)_2 \\ CH_2\cdot CH_2\cdot NMe_3\cdot OH \end{array} \quad \text{(III.)} \qquad C_8H_6O_3{<}\begin{array}{l} CH{:}CH\cdot C_6H_3(NO_2)_2 \\ CH{:}CH_2 \end{array} \quad \text{(IV.)}$$

The alternative view of the constitution of anhydrocotarnine-2:4-dinitrotoluene, namely:

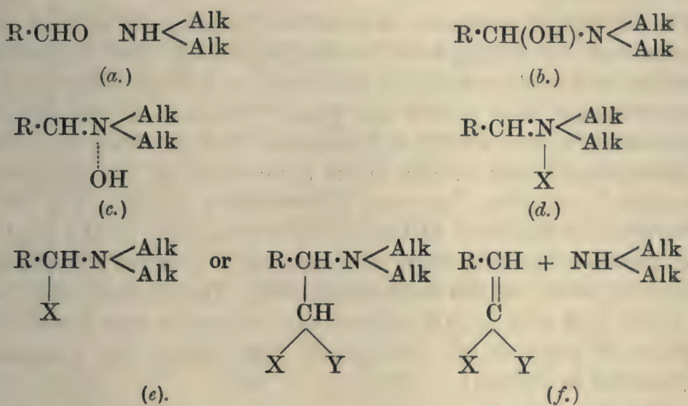
$$CH_2{:}O_2{:}C_6H(OMe){<}\begin{array}{l} CH{:}CH\cdot C_6H_3(NO_2)_2 \\ CH_2\cdot CH_2\cdot NHMe \end{array} \quad \text{(A)}$$

is clearly proved to be incorrect, since the methiodide of the base correctly represented by the structure (I) is a quite different substance from the hydriodide of the stilbene derivative (II). There can be little doubt that the condensation products of cotarnine with other nitrotoluenes are also derivatives of benzylhydrocotarnine.

It is a matter of considerable interest that the bases produced from cotarnine and di- or tri-nitro-compounds are readily decomposed on boiling with glacial acetic acid, the original components being regenerated by the addition of a molecule of water. This hydrolysis can also be effected by alcoholic potassium hydroxide, and is probably not due to the intermediate formation of the open-chain substance (A), since the base (II) is not appreciably changed when boiled for an hour with acetic acid. The simplest scheme which represents the decomposition is the reverse of that formulated for the synthesis, but it may well be that the acid causes the group $\cdot CH_2\cdot$ to migrate to the nitrogen, a process which it is clear would be at once followed by the formation of a cotarninium salt and a dinitrotoluene.

The Mechanism of the Condensation Reactions of Cotarnine and other Pseudo-bases.

Dr. Lapworth has suggested to the authors an explanation of the condensation of aldehydes and methylene compounds in the presence of a secondary base (Knoevenagel reaction), which may be represented as follows:



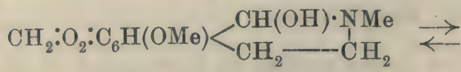
In the first stage free aldehyde (or ketone) and dialkylamine unite to form the carbinol (*b*), which is probably in all cases in equilibrium with the ammonium hydroxide (*c*). In ionising solvents, the equilibrium is naturally displaced in favour of this latter form.

The positive ion of (*c*) can unite with the negative residue of a substance H·X, where X is any group such as ·CN, $\cdot CH_2\cdot NO_2$, $\cdot CH_2\cdot C_6H_3(NO_2)_2$, $\cdot CH(CO_2Et)_2$, $\cdot CH_2\cdot COPh$, etc., and so produces the complex (*d*), which is very unstable, and changes to (*e*). When X is ·CN this represents the final stage, but in those cases where the substance H·X contains a reactive methylene group, that is, $CH_3\cdot X$ and CH_2XY, the further change to (*f*), with reproduction of the secondary base, occurs.

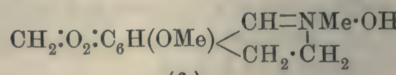
Finally, this unsaturated substance may add on another molecule of CH_2XY, a reaction completely analogous to the addition of ethyl sodiomalonate to $\alpha\beta$-unsaturated esters.

It is unnecessary to dilate on the probability of the above explanation, or to adduce specific chemical analogies for the various stages, but it may be stated that chemical literature contains experimental evidence for each of the changes involved. The spectroscopic investigations of Dobbie, Lauder, and Tinkler (Trans., 1903, **85**, 598) have clearly shown that cotarnine is an equilibrium mixture of carbinol (α) and ammonium hydroxide (β), the latter predomin-

ating in alcoholic solution, whilst evidence for the open-chain aldehyde-imine structure is entirely lacking:,



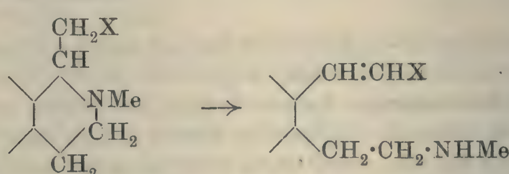
(α.)



(β.)

The proved (β) structure of cotarnine in alcoholic solution corresponds with (*c*) in Lapworth's explanation of the Knoevenagel reaction, and the products of condensation with substances of the type H·X have been shown (see above) to possess a hydrocotarnine constitution, and to correspond therefore with (*e*). This explanation is consequently very simple in its application to the reactions of cotarnine,* requiring but one intermediate phase. The change (*e*) to (*f*) does not occur in the case of the majority of the condensation products of cotarnine, and the only example in which we suspect it is that of the condensation with dinitrophenylacetic ester (p. 2132), and even in this instance the evidence is very inconclusive.

With hydrocotarnine compounds the change in question is represented as follows:



The probable reason for the fact that unsaturated substances of this type are not produced must be sought in the stability of the ring structure.

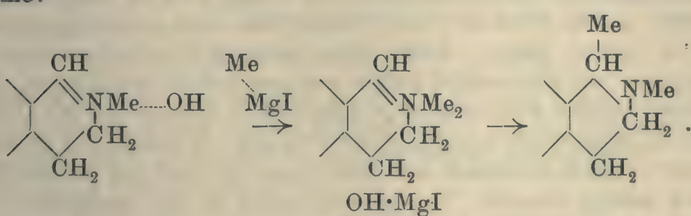
On the basis of the above hypothesis, cotarnine, and, indeed, all pseudo-bases, should condense with any substance which is capable of giving rise to a negative ion, unless the reaction is sterically hindered, or is in opposition to the laws of thermodynamics. Various considerations will, however, affect the stage which the resulting product reaches; thus, for example, with acids there is very little or no tendency for the acid radicle to migrate to carbon. Acid amides and imides are probably partly ionised in solution, and should therefore condense with cotarnine. In point of fact a number of substances described as molecular compounds of cotarnine and amides and imides have recently been produced (Knoll & Co.,

* Cotarnine is taken throughout this discussion as an example, but the observations are intended to apply to all pseudo-bases where there is a possibility of migration of groups from the nitrogen to carbon.

D.R.-P. 232785). We have examined one of them, namely, that from cotarnine and phthalimide, and our analysis proves that the substance is anhydrocotarninephthalimide, loss of water having occurred. Although this compound is immediately decomposed by acids with the production of cotarninium salts and phthalimide, we regard it as analogous to ethoxyhydrocotarnine, that is, as phthaloylaminohydrocotarnine.

In those cases where an agent has been found necessary to effect the condensation of a pseudo-base with a third substance, this agent can have no effect on the base, except to suppress its ionisation and so hinder the reaction. The agent facilitates the condensation by enabling the third substance, most probably a feeble pseudo-acid, to give rise to a negative ion. The condensation of cotarnine with *o*- or *p*-nitrotoluene in the presence of sodium ethoxide (see p. 2123) probably belongs to this category.

In conclusion, it may be mentioned that the action of magnesium alkyl haloids on cotarnine and other pseudo-bases must probably be explained by a similar idea, which is expressed in the following scheme:



EXPERIMENTAL.

Anhydrocotarninenitromethane,

$$CH_2{:}O_2{:}C_6H(OMe){<}\begin{matrix}CH_2{\cdot}NO_2 \\ | \\ CH{-}NMe \\ \quad\;\; | \\ CH_2{\cdot}CH_2\end{matrix}$$

This substance is prepared with great facility according to the following method:

A solution of cotarnine (20 grams) in ethyl alcohol (40 c.c.) is mixed with nitromethane (15 grams), when the temperature rises, and in about half a minute the condensation product crystallises from the liquid. After remaining an hour at the room temperature, the crystals are separated and washed with alcohol, a further quantity being obtained from the mother liquors on standing for a few days. The substance is readily soluble in boiling ethyl alcohol, and crystallises on cooling in fine, colourless prisms, melting at 129°. On analysis of a specimen dried in a vacuum:

0·1191 gave 0·2441 CO_2 and 0·0588 H_2O. C=55·8; H=5·5.

$C_{13}H_{16}O_5N_2$ requires C=55·7; H=5·7 per cent.

A characteristic property of the substance is the formation of a very sparingly soluble hydrochloride. This crystallises in needles, and can be dissolved in a large excess of water. No trace of a benzoyl derivative could be isolated, whether the benzoylation was carried out with benzoyl chloride in aqueous alkaline or pyridine solution.

Picrate:—The base was dissolved in acetic acid, and the solution diluted with water and treated with picric acid. The yellow precipitate was collected, and crystallised from a mixture of methyl ethyl ketone and ethyl alcohol. Long, bright yellow, slender needles were obtained, which melted at 136—137°. On analysis the substance exploded with violence in the tube, so that a high result was always obtained in a nitrogen determination.

Action of Methyl Iodide on Anhydrocotarninenitromethane.

The finely powdered substance was boiled with an excess of pure methyl iodide, when the colourless crystals were gradually replaced by a yellow gum. After three hours this transformation was complete, and the methyl iodide was removed by distillation. The gummy residue was completely dissolved in boiling methyl alcohol, and the deep yellow solution allowed to cool. A quantity of intensely yellow crystals separated, and these were collected and recrystallised from methyl alcohol. The melting point of this methiodide was 229°. A specimen that had been recrystallised five times was dried in a vacuum, and analysed:

0·1381 gave 0·2125 CO_2 and 0·0655 H_2O. C=41·9; H=5·3.
0·1178 „ 0·1800 CO_2 „ 0·0560 H_2O. C=41·7; H=5·3.
0·1221 „ 0·0659 AgI. I=29·2.

$C_{15}H_{21}O_5N_2I$ requires C=41·3; H=4·8; I=29·1 per cent.

These results show that this substance is probably a *methylanhydrocotarninenitromethane methiodide*, and has the constitution:

$$C_8H_6O_3<\begin{matrix}CH{:}CH\cdot NO_2\\ CH_2\cdot CH_2\cdot NMe_3I\end{matrix}.$$

Proof of the correctness of this view is afforded by the examination of the products of its decomposition with alkalis. The methiodide was converted into the corresponding methochloride in the usual way by heating with silver chloride in aqueous solution, and on the addition of potassium hydroxide, trimethylamine was very readily evolved. The solution was distilled, the distillate acidified with hydrochloric acid, concentrated, and treated with

platinic chloride, when a platinichloride was obtained, which melted at 238—239°, and possessed all the characteristics of trimethylamine platinichloride. We were unable to isolate the neutral decomposition product.

When the methiodide melting at 229° had been separated from the methyl-alcoholic mother liquor, another substance began to crystallise. It was at once obvious that this was a second methiodide, since it was only pale yellow in colour, and had a characteristic property of absorbing water of crystallisation. The substance was purified by many crystallisations from methyl alcohol, and was obtained in almost colourless, prismatic needles, which lose solvent of crystallisation at 110—115°, and then melt at 199°. The analytical results for this substance were unsatisfactory, since it loses some of its solvent of crystallisation on drying in the air. In order to obtain the percentage of iodine in the dry substance, determinations of the loss on heating and of the iodine were made with the same air-dried specimen:

0·7882 lost, at 120°, 0·0180 solvent. $CH_4O = 2·3$ per cent.

0·1253 gave 0·0681 AgI. $I = 30·0$ (calculated for anhydrous substance).

$C_{14}H_{19}O_5N_2I$ requires $I = 30·0$ per cent.

When a little of the substance is ground up with water, it swells up and becomes a mass of pale yellow needles. It was recrystallised from water, dried in air, and the loss on heating determined:

0·9774 lost 0·0516 H_2O. $H_2O = 5·2$.

$C_{14}H_{19}O_5N_2I,H_2O$ requires $H_2O = 4·1$ per cent.

The substance melted at 105—115°, then re-solidified, and melted at 196—198°. On decomposition of this methiodide with alkali practically no volatile base was obtained; it gave the merest trace of a platinichloride, melting at 228°.

All the above observations are in agreement with the hypothesis that this second methiodide is the normal methiodide of anhydrocotarninenitromethane. It can be represented by either of the following formulæ, but we prefer the first, and regard the production of the yellow methiodide as occurring by the opening of the *iso*quinoline ring:

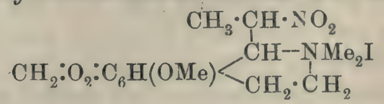
$$C_8H_6O_3 \begin{array}{l} \phantom{<}CH_2·NO_2 \\ \phantom{<}\mid \\ \diagup CH-NMe_2I \\ \phantom{<}\mid \qquad\quad \mid \\ \diagdown CH_2·CH_2 \end{array} \qquad\qquad C_8H_6O_3<\begin{array}{l} CH:CH·NO_2 \\ CH_2·CH_2·NMe_2HI \end{array}$$

(I.) (II.)

Further experiments have been made, and will be made, on this base, in respect, for example, of its reduction products, but it is hoped that they will form the subject-matter of a future communi-

cation. In the meantime we have represented the substance as a derivative of hydrocotarnine, the chief arguments in favour of this view being its lack of visible colour and the formation of a normal methiodide.

Anhydrocotarninenitroethane Methiodide,



Cotarnine (6 grams) was dissolved in alcohol, and the solution boiled for ten minutes with nitroethane (1·9 grams). On evaporating a portion of the solution, a gummy residue was obtained, and this could not be induced to crystallise. That a condensation had occurred was proved by the following experiments. In the first place, a solution of the gum in dilute hydrochloric acid gave, on addition of picric acid, a bright yellow precipitate of a picrate, which crystallised from acetone in greenish-yellow prisms, melting at 114—116°. This could not be cotarnine picrate, and was therefore the picrate of a condensation product. The main portion of the gum was treated with boiling methyl iodide, when a methiodide was produced, and became solid in contact with cold methyl alcohol. After separation, the substance was crystallised from methyl alcohol, and was obtained in pale yellow, rectangular plates, melting and decomposing, with slight previous darkening, at 216—218°. This melting point led us to suspect that the substance was cotarnmethine methiodide, which melts at 217—219°; but a careful comparison of the two substances clearly proved that this was not the case; also, an intimate mixture of these methiodides melted at 196—200°.

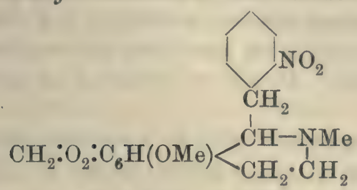
On analysis of a specimen dried in a vacuum:

0·1409 gave 0·0766 AgI. I = 29·4.

$C_{15}H_{21}O_5N_2I$ requires I = 29·1 per cent.

Since in the case of anhydrocotarninenitroethane only one methiodide is isolated, it probably corresponds with the simple methiodide of anhydrocotarninenitromethane, a supposition which is in agreement with its pale yellow colour and its percentage of iodine. The constitution of the substance is probably correctly represented at the head of the section, but it is impossible to be sure of this until the products of its decomposition by alkalis are examined. A volatile base is produced in only very small quantities in this reaction.

Anhydrocotarnine-2-nitrotoluene,



A condensation can be effected between cotarnine and *o*-nitrotoluene in the absence of any condensation agent, but the process is slow, and results in a small yield of the desired product. The use of sodium ethoxide was found to have a large effect in facilitating the preparation of this substance, and the following were the conditions employed:

A solution of sodium ethoxide (0·5 gram of sodium) in alcohol (50 c.c.) was added to a mixture of cotarnine (5 grams) and *o*-nitrotoluene (10 grams), and the liquid was then kept in the cold for twenty-four hours. The yellow solution was then treated with dilute hydrochloric acid, and extracted with ether to remove the excess of nitrotoluene. The aqueous layer was separated, and, after saturating with sodium acetate, again extracted with ether. In this way the condensation product is separated from cotarnine, because the latter is not liberated from its salts by sodium acetate.

The pale yellow ethereal solution was washed with water, dried with potassium carbonate, and distilled, leaving a viscid, yellow oil, which could not be induced to crystallise. It was dissolved in alcohol, and treated with a solution of picric acid in the same solvent, when after a short time a very sparingly soluble picrate crystallised from the solution in intense yellow prisms. The substance so obtained was quite pure, as the following analysis indicates, and very little is to be gained by the crystallisation of this picrate, since the only solvent in which it is sufficiently soluble for the purpose is acetic acid, and a certain amount of decomposition ensues. A specimen of this derivative was later prepared from the pure base, and found to melt at 203—205°:

0·1275 gave 12·7 c.c. N_2 at 14° and 752 mm. N = 11·5.

$C_{24}H_{21}O_{12}N_5$ requires N = 11·9 per cent.

The picrate was then decomposed by very dilute sodium hydroxide, whilst the base produced was simultaneously extracted with ether. This process was accomplished in a very much shorter time when the alkali was repeatedly changed. In any case, the picrate is difficult to decompose, especially by ammonia or potassium hydroxide.

The ethereal solution of anhydrocotarnine-2-nitrotoluene was washed with water, dried with potassium carbonate, and distilled. The residue now became solid on scratching the sides of the containing vessel, and the substance was twice recrystallised from not too much methyl alcohol. It was so obtained in pale yellow prisms, melting at 75°.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1235 gave 0·2891 CO_2 and 0·0650 H_2O. C=63·8; H=5·8.

$C_{19}H_{20}O_5N_2$ requires C=64·0; H=5·6 per cent.

This compound is readily soluble in ethyl alcohol or ether, more sparingly so in methyl alcohol or light petroleum; from a hot solution in the latter solvent it is deposited in flat prisms, which are all but colourless.

The hydrochloride is sparingly soluble in water, and crystallises, in perfectly colourless micro-prisms of rather indefinite shape, when the solution of the base in concentrated hydrochloric acid is diluted. The double salts, for example, the platinichloride, aurichloride, and mercurichloride, are very sparingly soluble amorphous precipitates. The substance dissolves readily in dilute sulphuric acid, but the sulphate soon crystallises from the solution, and consists of colourless, rectangular prisms.

When a warm solution of the hydrochloride is treated with zinc, reduction readily occurs, and the pale yellow liquid resulting on the addition of sodium nitrite contains a diazonium salt, which yields intense red azo-dyes with β-naphthol and "R-salt" in alkaline solution.

It is of interest to note that this base is not decomposed by boiling with acetic acid, and in this respect it differs from the dinitro-derivatives shortly to be described.

Anhydrocotarnine-4-nitrotoluene,

$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad CH_2\cdot C_6H_4\cdot NO_2 \\ \qquad\qquad\qquad\qquad\qquad | \\ CH_2{:}O_2{:}C_6H(OMe) \begin{array}{l} \diagup CH-NMe \\ \qquad\qquad | \\ \diagdown CH_2\cdot CH_2 \end{array} \end{array}$$

The experience gained in dealing with the foregoing substance was applied in condensing cotarnine with *p*-nitrotoluene, since it was found that the reaction was impracticably slow without a condensing agent.

A mixture of cotarnine (10 grams), *p*-nitrotoluene (15 grams), and alcohol (100 c.c. containing sodium ethoxide from 1 gram of sodium) was gently warmed until a clear solution was obtained, and then allowed to remain without further heating for a day. The liquid was diluted with water, acidified with hydrochloric acid, and

separated by filtration from the unchanged *p*-nitrotoluene. The addition of ammonia to the filtrate produced a milky solution, from which a quantity of a crystalline substance gradually separated. This was collected, and crystallised, first from methyl, and then from ethyl alcohol.

On analysis of a specimen dried in a vacuum over sulphuric acid:

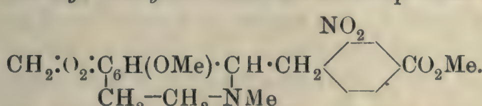
0·1331 gave 0·3138 CO_2 and 0·0711 H_2O. C = 64·3; H = 5·9.

$C_{19}H_{20}O_5N_2$ requires C = 64·0; H = 5·6 per cent.

Anhydrocotarnine-4-nitrotoluene is readily soluble in boiling ethyl alcohol, but sparingly so in the cold, and separates in aggregates of leaf-shaped crystals. It melts at 121—122°, without decomposition. Although it is a pale yellow substance, it forms colourless salts, of which the hydrochloride and sulphate are sparingly soluble in water, the former crystallising from a hot aqueous solution in glistening, elongated prisms. The platinichloride is an amorphous precipitate, which changes to yellow needles on boiling the solution. A *picrate* very sparingly soluble in alcohol is produced in canary-yellow prisms when picric acid is added to a hot alcoholic solution of the base. This derivative melts at 188—190°.

The observations on the stability in boiling acetic acid and on the formation of azo-dyes that were made with anhydrocotarnine-2-nitrotoluene (see above), apply also to anhydrocotarnine-4-nitrotoluene.

Methyl Anhydrocotarnine-o-*nitro*-p-*toluate*,



Methyl *o*-nitro-*p*-toluate is mentioned by Noad (*Annalen*, 1847, **63**, 297), who describes it as a crystalline substance. We have prepared it by boiling *o*-nitro-*p*-toluic acid with 5 per cent. methyl-alcoholic sulphuric acid for half an hour. The ester crystallises well from methyl alcohol in long, colourless needles, and melts sharply at 51°:

0·1130 gave 0·2282 CO_2 and 0·0478 H_2O. C = 55·1; H = 4·7.

$C_9H_9O_4N$ requires C = 55·4; H = 4·6 per cent.

Although it is a mononitrotoluene derivative, the negative effect of the carbomethoxy-group is so great that the condensation with cotarnine can be accomplished without the use of sodium ethoxide. In carrying out this reaction a solution of methyl *o*-nitro-*p*-toluate (10 grams) and cotarnine (10 grams) in methyl alcohol (65 c.c.) was boiled for three hours. The solution was then cooled, and allowed to remain in the ice-chest overnight. The substance gradually crystallised from the yellowish-brown liquid, and very

little of the base remained in the mother liquor. It was collected, washed with methyl alcohol, dried, and crystallised by adding methyl alcohol, in which it is very sparingly soluble, to its saturated solution in boiling methyl ethyl ketone. Almost colourless, prismatic crystals were obtained, and after recrystallisation melted at 146°:

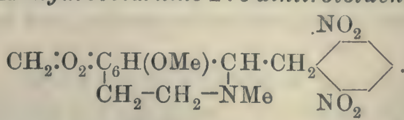
0·1500 gave 0·3360 CO_2 and 0·0741 H_2O. C=61·1; H=5·5.

$C_{21}H_{22}O_7N_2$ requires C=60·9; H=5·3 per cent.

The substance yields readily soluble salts with mineral acids, and the usual not very characteristic, sparingly soluble double salts. It is not changed on boiling with glacial acetic acid for a short time. The picrate is obtained in canary-yellow prisms, melting at 163—170°, by adding a methyl-alcoholic solution of picric acid to a solution of the base in methyl ethyl ketone.

When the base is boiled with alcoholic potassium hydroxide it gradually dissolves, and is not reprecipitated on the addition of water. That the ester has been hydrolysed in a normal manner is proved by the fact that on the addition of hydrochloric acid and aqueous picric acid to the solution a bright yellow picrate is precipitated. This can be recrystallised from a large quantity of a mixture of equal parts of acetone and methyl alcohol, and occurs in microscopic prisms, melting at 183—185°. Its formulation as anhydrocotarnine-*o*-nitro-*p*-toluic acid picrate is justified by its immediate and complete solubility in sodium carbonate, and by the conversion into methyl anhydrocotarnine-*o*-nitro-*p*-toluate picrate, a change which can be effected by the agency of a solution of picric acid in methyl-alcoholic hydrochloric acid. The melting point of the picrate falls to 168° with slight previous softening, it is no longer soluble in sodium carbonate, and on treatment with alkali and ether is decomposed, so that the original ester base can be recovered from the ethereal solution.

Anhydrocotarnine-2:6-*dinitrotoluene*,



A solution of 2:6-dinitrotoluene (3·6 grams) in as little methyl alcohol as possible was added to cotarnine (4·8 grams) and methyl alcohol (30 c.c.), and the mixture boiled for five minutes. After some time the deep brownish-red solution began to deposit a crystalline substance. In subsequent operations this separation was very much facilitated by seeding. The crystals were collected, washed with methyl alcohol, and recrystallised from ethyl alcohol. The methyl-alcoholic mother liquor and washings contain a further

quantity of the substance, which can be obtained by the partial evaporation of the solvent. The new substance crystallises from ethyl alcohol in bright yellow prisms, melting at 112—114°.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1347 gave 0·2824 CO_2 and 0·0578 H_2O. C = 57·2; H = 4·8.

$C_{19}H_{19}O_7N_3$ requires C = 56·8, H = 4·7 per cent.

The substance is readily soluble in boiling ethyl alcohol and in chloroform or benzene. When boiled with acetic acid, the colourless solution becomes yellow, and 2:6-dinitrotoluene (m. p. 60°) and cotarnine acetate are produced.

The *picrate* is obtained by mixing a solution of the base in methyl ethyl ketone with an alcoholic solution of picric acid. It is sparingly soluble in most solvents, and forms canary-yellow prisms, melting at 153—155°.

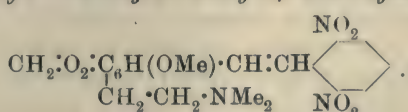
Methiodide.—The base was boiled with an excess of methyl iodide for ten minutes, when a methiodide was produced, which crystallised from methyl alcohol in light yellow prisms, melting at 210—212°. Although the substance had all the characteristics of a pure compound, and its melting point was not raised by further crystallisation, yet, as the following results show, the percentage of iodine found was always high:

0·1390 gave 0·0627 AgI. I = 24·4.
0·1215 „ 0·0562 AgI. I = 25·0.

$C_{20}H_{22}O_7N_3I$ requires I = 23·4 per cent.

We are unable to suggest any explanation of this anomaly, since we regard the constitution of the substance as proved by its decomposition with alkalis, as described in the next section.

2′:6′-*Dinitro-2-methoxy-*3:4-*methylenedioxy-*6-β-*dimethylamino-ethylstilbene*,



Anhydrocotarnine-2:6-dinitrotoluene methiodide was dissolved in hot water, and heated on the steam-bath with an excess of freshly precipitated silver chloride during a quarter of an hour. Silver iodide was produced, and the solution of the methochloride was collected and treated with excess of sodium hydroxide. After gently warming for a few minutes, the copious, brown precipitate which was formed was collected, washed, dried, and crystallised from methyl alcohol.

When prepared in this way the substance has a brilliant, orange-red colour, and occurs in lozenge-shaped plates, melting at 93—95°,

but occasionally yellow crystals melting at 75° were obtained; these contained solvent of crystallisation, and on remaining overnight in the air, reverted to the red variety, and melted at 94°.

On analysis of a specimen dried in a vacuum over sulphuric acid:

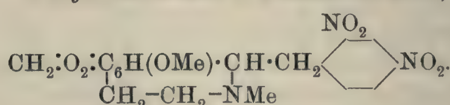
0·1200 gave 0·2568 CO_2 and 0·0551 H_2O. C=58·3; H=5·1.

$C_{20}H_{21}O_7N_3$ requires C=57·8; H=5·0 per cent.

Considerable care was necessary in carrying out the combustion, as the compound tends to decompose with violence.

This substance is a base entirely analogous to the corresponding compound from 2:4-dinitrotoluene. It is sparingly soluble in cold methyl alcohol, but readily soluble in ethyl acetate or benzene. The hydrochloride is sparingly soluble in water or cold alcohol, readily in boiling alcohol, and on the addition of picric acid to the solution a crystalline picrate is obtained.

Anhydrocotarnine-2:4-*dinitrotoluene*,



This substance was prepared in a manner exactly similar to that described in the case of the 2:6-isomeride (see above), but it was obtained with greater readiness, and in practically quantitative yield.

When equimolecular quantities of cotarnine and 2:4-dinitrotoluene were boiled together in methyl-alcoholic solution, separation of the yellow crystals of the condensation product usually occurred in a few minutes, and while the liquid was hot. The crystalline precipitate was separated from the cooled solution by filtration, and the substance purified by crystallisation from a mixture of chloroform and methyl alcohol. The yellow prisms so obtained melt at 145—146° with vigorous decomposition.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1194 gave 0·2477 CO_2 and 0·0518 H_2O. C=56·6; H=4·8.

$C_{19}H_{19}O_7N_3$ requires C=56·8; H=4·7 per cent.

The substance is sparingly soluble in methyl or ethyl alcohol and in benzene, readily so in chloroform or pyridine. The base itself and all its derivatives are more sparingly soluble than the corresponding isomerides from 2:6-dinitrotoluene.

The solution of the compound in dilute hydrochloric acid is pale yellow, and the addition of ammonia regenerates the unchanged substance as a light yellow, amorphous precipitate, rapidly becoming crystalline. The same applies to the solution of the base in cold

acetic acid; if, however, this solution is boiled, then decomposition ensues, with production of cotarnine (picrate, m. p. 141—143°) and dinitrotoluene (m. p. 69°). This decomposition is discussed in the introduction to the paper.

Precipitates of double salts are obtained when the appropriate reagents are added to a solution of the base in dilute acid, but they are not specially characteristic.

Methiodide.—This derivative was obtained by boiling the finely powdered substance with an excess of methyl iodide. The salt was quickly formed, and was found to crystallise from methyl alcohol in orange prisms. If quickly heated the substance will melt and evolve gas, even below 180°, but when the melting point is taken slowly it is found to be 244—245°, with gradual decomposition above 200°. Great difficulty was experienced in obtaining a pure specimen of this methiodide, although, as in the case of the 2:6-dinitro-compound, the external characteristics were those of a single substance:

0·1748 gave 0·0738 AgI. I = 22·8.

$C_{20}H_{22}O_7N_3I$ requires I = 23·4 per cent.

2′:4′-Dinitro-2-methoxy-3:4-methylenedioxy-6-β-dimethylamino-ethylstilbene, $C_8H_6O_3{<}{\begin{smallmatrix}CH:CH\cdot C_6H_3(NO_2)_2\\ CH_2\cdot CH_2\cdot NMe_2\end{smallmatrix}}$.

The methiodide of anhydrocotarnine-2:4-dinitrotoluene was converted into the methochloride by warming with silver chloride in aqueous solution, and after filtration an excess of sodium hydroxide was added. The dense, orange-coloured precipitate was collected, dried, and crystallised from ethyl acetate. It separates in long, reddish-brown prisms, melting at 155°.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1335 gave 0·2833 CO_2 and 0·0656 H_2O. C = 57·8; H = 5·4.
0·1145 „ 0·2440 CO_2 „ 0·0500 H_2O. C = 58·1; H = 4·8.

$C_{20}H_{21}O_7N_3$ requires C = 57·8; H = 5·0 per cent.

This substance is very sparingly soluble in hot methyl alcohol, but easily dissolves in boiling chloroform or ethyl acetate. The hydrochloride is very sparingly soluble in water and alcohol; it crystallises from aqueous alcohol in yellow plates. A hot aqueous-alcoholic solution of the hydrochloride on treatment with picric acid deposits lozenge-shaped crystals of a yellow picrate, which melt at 185—187°.

Hydriodide.—This derivative is of considerable interest in that the fact of its difference from the methiodide of anhydrocotarnine-2:4-dinitrotoluene proves that the latter base has a hydrocotarnine

structure. It is obtained as a yellow precipitate by mixing a solution of the base in glacial acetic acid with a dilute alcoholic solution of hydriodic acid, and the yellow crystals on boiling with alcohol are converted into brilliant red prisms. The substance was crystallised from formic acid, and separated at first as the red variety, which could be obtained in a pure condition. When, however, a certain temperature was reached, the yellow form began to crystallise in glistening flakes. It appears that the yellow form separates at low temperatures, and it can always be converted into the more stable red form by warming in the presence of any solvent in which the substance is partly soluble. The yellow crystals were not obtained free from the red; the latter melt and decompose at 245—248°, and gave the following result on analysis:

0·1166 gave 0·0498 AgI. I = 23·1.

$C_{20}H_{22}O_7N_3I$ requires I = 23·4 per cent.

Methiodide.—When the base is boiled for five minutes with methyl iodide a methiodide is produced, which is exceedingly sparingly soluble in almost all solvents. The substance was prepared in considerable quantity, and purified by extraction with boiling ethyl acetate, which removed any unaltered base. For analysis a small specimen was obtained in a pure condition by crystallisation from a large quantity of methyl alcohol. It consists of orange-yellow, rectangular prisms, which melt at 244—246°:

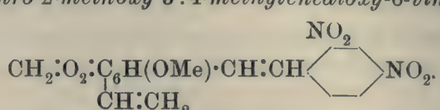
0·1575 gave 0·0661 AgI. I = 22·7.

$C_{21}H_{24}O_7N_3I$ requires I = 22·8 per cent.

The corresponding *methochloride* was produced by heating this methiodide in aqueous suspension with freshly precipitated silver chloride. The filtered solution deposits on cooling a crystalline precipitate resembling very much lead iodide. The methochloride, although, as is usual, more soluble than the methiodide, is still sparingly soluble in water and alcohol. It is stable in the presence of alkaline hydroxides, so that it was necessary to resort to the use of silver oxide in order to obtain the quaternary ammonium base.

In the experiment which is described below, it was found to be more convenient to employ the methiodide direct.

2′ : 4′-*Dinitro*-2-*methoxy*-3 : 4-*methylenedioxy*-6-*vinylstilbene*,



The methiodide described above (5 grams) was completely dissolved in the least possible quantity of hot water (5 litres), and

digested on the steam-bath with silver oxide (from 10 grams of silver nitrate) during six hours. The orange-coloured solution was filtered, and evaporated until crystallisation at the surface commenced. The solution had the odour of trimethylamine, and was filtered from a small quantity of a neutral, red substance. On cooling, a new substance crystallised in golden spangles, which under the microscope are seen to consist of irregular, hexagonal prisms. On heating, the compound turns red at 120—130°, and then decomposes at 164—166°. Its whole behaviour harmonises with the view that it is a methyl hydroxide, and one which evidently possesses considerable stability. It dissolves in hot water, and the yellow solution gives a precipitate of the characteristic methochloride with hydrochloric acid. The stability of this ammonium base is remarkable, and we experienced great difficulty in causing its fission into trimethylamine and the neutral stilbene derivative. This could be accomplished, at the expense of great loss through decomposition, by heating the substance in the dry state. The method finally adopted was to boil a concentrated aqueous solution for many hours, when a slow decomposition occurred, involving the production of trimethylamine and a red powder, which was separated by filtration. The substance was purified by boiling with water to remove a small quantity of unaltered methyl hydroxide, and, after drying, crystallised from acetone. The crystals are tiny, rectangular prisms, melting at 162—163°. When first obtained they are brownish-yellow, but on drying at 90° they become deep, brilliant red. The substance is quite devoid of basic properties, and crystallises unchanged from acetic acid. It is fairly soluble in hot acetone, and sparingly so in alcohol.

On analysis of a specimen dried at 90°:

0·1173 gave 0·2535 CO_2 and 0·0441 H_2O. C = 58·9; H = 4·2.

$C_{18}H_{14}O_7N_2$ requires C = 58·4; H = 3·8 per cent.

In order to be quite sure of the constitution of this neutral substance, its synthesis was accomplished by the following process:

Cotarnone (2 grams) and 2:4-dinitrotoluene (2 grams) were melted together, and warmed on the water-bath for an hour with three drops of piperidine. The mass of red crystals which resulted was dissolved in boiling acetic acid, and on cooling the substance separated in aggregates of micro-prisms, resembling chromic acid in appearance. The substance melted, after recrystallisation, at 163—164°, and its melting point was unaltered by admixture with the substance obtained as above from anhydrocotarninedinitrotoluene:

0·1409 gave 0·3040 CO_2 and 0·0497 H_2O. C = 58·8; H = 3·9 per cent.

Methyl Anhydrocotarnine-2:4-dinitrophenylacetate,

$$\underset{\displaystyle CH_2\cdot CH_2\cdot NHMe}{CH_2{:}O_2{:}C_6H(OMe)}\cdot CH{:}C(CO_2Me)\cdot C_6H_3(NO_2)_2 \quad (?).$$

This substance was prepared by the condensation of methyl dinitrophenylacetate (Borsche, *Ber.*, 1909, **42**, 1310) with cotarnine under the following conditions. A mixture of the ester (2 grams) and an equal quantity of cotarnine was boiled for five minutes with enough methyl alcohol to dissolve it. The solution acquires a deep black colour, and on cooling deposits jet black crystals, which were collected and dried. The substance was recrystallised from methyl alcohol, and obtained in black prisms, which show green iridescence and melt at 150—151° with vigorous decomposition.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1310 gave 0·2649 CO_2 and 0·0561 H_2O. C=55·1; H=4·7.
$C_{21}H_{21}O_9N_3$ requires C=54·9; H=4·5 per cent.

The black colour of this substance, which is so characteristic, is only observed in the crystalline condition; when rubbed on paper, a brown streak is produced, and cold methyl alcohol is coloured red by contact with the solid. No stable salts could be prepared, since in contact with strong or dilute acids it is at once decomposed with production of cotarnine and of methyl dinitrophenylacetate (m. p. 82°). Further, as seen below, no methiodide could be obtained. It is in consideration of these facts, which clearly show its lack of resemblance to anhydrocotarnine-2:4-dinitrotoluene, that we have assigned the open-chain structure, figured above, to this substance.

Action of Methyl Iodide.—The black condensation product was boiled for an hour with an excess of methyl alcohol and methyl iodide. On cooling, a quantity of reddish-brown crystals were obtained, and these were collected, drained on porous porcelain, and recrystallised from methyl alcohol. The faintly yellow crystals were examined under the microscope, and found to consist of hexagonal plates, and no crystals of other shape could be detected. The melting point was 210—213° (decomp.), and was unaltered by the recrystallisation of the substance. It is evidently a pure compound, but we have been unable to identify it. The percentage of iodine found was 35·5, which is much too high for the normal methiodide (21·1), and agrees better for a substance like hydrocotarnine methiodide or hydriodide. These compounds were prepared in order to effect a direct comparison, but the result showed that the unidentified methiodide was a different substance.

Hydrocotarnine Hydriodide.—This salt was prepared by the addition of concentrated aqueous hydriodic acid to a solution of

hydrocotarnine in alcohol. The substance crystallises from methyl alcohol in colourless needles, melting at 195—196°.

Hydrocotarnine Methiodide.—Hydrocotarnine reacts with methyl iodide in the cold, and the product crystallises well from methyl alcohol in magnificent prisms. This derivative melts without decomposition at 206—207°.

On analysis of a specimen dried in a vacuum:

0·1009 gave 0·0650 AgI. I = 34·8.

$C_{13}H_{18}O_3NI$ requires I = 35·0 per cent.

Anhydrocotarnine-2:4:6-trinitrotoluene,

$$CH_2{:}O_2{:}C_6H(OMe)\cdot CH\cdot CH_2\cdot C_6H_2(NO_2)_3$$
$$CH_2-CH_2-NMe$$

Cotarnine condenses with trinitrotoluene as readily as with nitromethane, and the preparation of the condensation product is a very simple matter, and merely consists in grinding up trinitrotoluene with an alcoholic solution of an equimolecular quantity of cotarnine. As soon as the substances come into contact, the orange-yellow compound commences to crystallise, and the reaction is complete in a few minutes. The crystals are collected, and dissolved in cold chloroform, and, on adding methyl alcohol to the solution, the new compound is obtained in a pure condition as intense yellow prisms, melting, when slowly heated, at 130° with explosive decomposition. This property rendered the analysis of the substance a matter of some difficulty, and high results were obtained, both for carbon and hydrogen. This could scarcely be avoided, since even when the substance was mixed with a large excess of copper oxide an explosion occurred, and nitrous fumes could be seen in the bulbs.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1224 gave 0·2321 CO_2 and 0·0517 H_2O. C = 51·7; H = 4·7.

$C_{19}H_{18}O_9N_4$ requires C = 51·1; H = 4·0 per cent.

The substance is sparingly soluble in most neutral solvents, but readily dissolves in cold chloroform, giving a brownish-yellow solution. The solutions in hot alcohol or ethyl acetate are, however, intensely red, and this property is so characteristic that although the trinitro-compound is practically insoluble, yet alcohol is coloured red by contact with it in the cold.

The base dissolves in concentrated hydrochloric acid, forming a pale yellow solution, which remains clear on dilution with water; on keeping, however, long, yellow needles of the hydrochloride crystallise out, and may be recrystallised from warm dilute hydrochloric acid. If the solution of the hydrochloride is boiled, trinitrotoluene is obtained, but the process is not a smooth one. When

the pale yellow solution of the base in glacial acetic acid is boiled, a complete decomposition ensues, with the production of trinitrotoluene and cotarnine. The former crystallised from the acetic acid solution in needles melting at 81°, whilst the latter was obtained in the form of its picrate (m. p. 141—143°) when the diluted and filtered mother liquor from this crystallisation was treated with picric acid.

Dianhydrodicotarnine-2 : 4 : 6-*trinitro*-m-*xylene*,

$$\begin{array}{l} CH_2{:}O_2{:}C_6H(OMe)\cdot CH\cdot CH_2\cdot C_6H(NO_2)_3\cdot CH_2\cdot CH{-}C_6H(OMe){:}O_2{:}CH_2 \\ \qquad CH_2{-}CH_2{-}NMe \qquad\qquad\qquad\qquad\qquad\qquad NMe\cdot C_2H_4 \end{array}$$

Cotarnine was condensed with trinitro-*m*-xylene under the following conditions: Finely powdered trinitro-*m*-xylene (10 grams) was boiled with methyl alcohol (300 c.c.) sufficiently long to dissolve the greatest possible amount of the substance, and then treated with cotarnine (20 grams) and boiled for a further ten minutes. The trinitro-compound gradually passed into solution, and when the brownish-red liquid was allowed to remain in the cold a quantity of crystals separated. These were collected and recrystallised from ethyl acetate, and then again by adding methyl alcohol to the solution of the substance in a little cold chloroform. Pale yellow prisms of rather indefinite shape were obtained. The substance melts at 153—154° with vigorous decomposition and slight previous darkening.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1270 gave 0·2660 CO_2 and 0·0630 H_2O. C = 57·1; H = 5·5.

$C_{32}H_{33}O_{12}N_5$ requires C = 56·5; H = 5·0 per cent.

The rather high results that were obtained in this analysis do not militate against the conclusions we have drawn with respect to its composition, since they were certainly due to the same cause as in the case of the substance from trinitrotoluene. The substance closely resembles the compound produced by the condensation of trinitromesitylene and cotarnine, which from an analytical point of view was very carefully investigated (see p. 2135).

Dianhydrodicotarninetrinitro-m-*xylene* is a base readily soluble in dilute acids, but does not form any very characteristic derivatives. The platinichloride and aurichloride are amorphous precipitates. When the almost colourless solution of the base in glacial acetic acid is boiled, it acquires a yellow colour, and, on cooling, colourless prisms of trinitroxylene separate. The filtrate from these crystals (which melted at 182°) gives on dilution and treatment with picric acid a yellow precipitate of a picrate, which crystallises from alcohol or water in silky needles, melting at 139—143°, and obviously consists of the picrate of cotarnine.

Dianhydrodicotarninetrinitromesitylene,

$$C_6Me(NO_2)_3<\begin{matrix}CH_2\cdot C_{12}H_{14}O_3N\\CH_2\cdot C_{12}H_{14}O_3N\end{matrix}.$$

In order to effect a condensation between cotarnine and trinitromesitylene, it is not sufficient to boil an alcoholic solution of these substances on the steam-bath; much more vigorous treatment is necessary. The reaction was carried out as follows:

Trinitromesitylene (1·5 grams) was added to a solution of cotarnine (2 grams) in methyl alcohol (10 c.c.). The mixture was boiled as vigorously as possible in a test-tube, and continuously stirred with a glass rod, while the alcohol was allowed to evaporate. The trinitro-compound gradually dissolved, and a stage was reached at which the whole of it had passed into solution. The boiling was continued for one or two minutes longer, and the liquid was then poured into cold water. A pale yellow solid, at first rather viscid, was precipitated. Several such experiments were carried out, and the combined products separated by filtration and treated with dilute hydrochloric acid, which dissolved the greater part of the solid, forming a soluble salt, and leaving undissolved a small quantity of trinitromesitylene, which was removed by filtration. The yellow solution was rendered alkaline with ammonia, and the crude precipitated base was separated, washed, dried, and crystallised from a mixture of acetone and methyl alcohol. After four crystallisations the substance was obtained in pale yellow, prismatic crystals, melting at 183—185°. This crystallisation is very wasteful, and most of the analyses were made of specimens having rather lower melting point; indeed, the slightly impure substance melts so sharply at 175—176° that we had at first assigned this melting point to the compound.

On analyses of specimens dried in a vacuum over sulphuric acid:

A. 0·1429 gave 0·2993 CO_2 and 0·0695 H_2O. C = 57·1; H = 5·4.
B. 0·1273 „ 0·2683 CO_2 „ 0·0640 H_2O. C = 57·4; H = 5·5.
C. 0·0675 „ 6·15 c.c. N_2 at 17° and 755 mm. N = 10·4.
D. In a determination of methoxyl by Perkin's modification of Zeisel's method, 0·1910 gave 0·1211 AgI. MeO = 8·4.

$C_{33}H_{35}O_{12}N_5$ requires C = 57·1; H = 5·0; N = 10·0; MeO = 8·9 per cent.

(A) melted at about 168°; (B) was recrystallised (A), and melted at 171°; (C) was the purest specimen, melting at 183—185°; (D) melted at 175—176°. This substance was also prepared, using ethyl alcohol as the solvent, in which the reaction was carried out. The product obtained was identical with that described above; it melted at 175—177°, and the melting point was not lowered when the

substance was mixed with an equal quantity of the compound produced in the reaction when methyl alcohol was employed as solvent:

0·1218 gave 0·2552 CO_2 and 0·0589 H_2O. C=57·1; H=5·3.

This result of of interest, inasmuch as the analytical results for the base seemed to agree fairly well with the theory that one molecule of cotarnine condenses with one of the trinitro-compound, and that one of the nitro-groups is replaced by methoxyl. That this is not the case is shown by the above experiment.

The salts of this substance are readily soluble in water, and the solutions are almost colourless. On boiling with glacial acetic acid, trinitromesitylene (m. p. 228°) was obtained, the reaction evidently being quite analogous to the similar decomposition of anhydrocotarninetrinitrotoluene.

Anhydrohydrastininenitromethane,

$$\begin{array}{l} CH_2{:}O_2{\cdot}C_6H_2\text{——}CH{\cdot}CH_2{\cdot}NO_2 \\ \qquad\quad\; CH_2{\cdot}CH_2{\cdot}NMe \end{array}$$

This substance, and also the condensation product with 2:4-dinitrotoluene, described in the next section, were prepared in order to show that hydrastinine is apparently as reactive as cotarnine towards nitro-compounds. Hydrastinine (1 gram) dissolved in methyl alcohol (5 c.c.) was treated with nitromethane (1 gram), and the solution boiled for one minute. On cooling, the substance separated in long, colourless needles, and was recrystallised from ethyl alcohol, in which it is sparingly soluble in the cold.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1220 gave 0·2567 CO_2 and 0·0650 H_2O. C=56·9; H=5·9.

$C_{12}H_{14}O_4N_2$ requires C=57·6; H=5·6 per cent.

The substance melts to a clear liquid at 121—122°. It is readily soluble in cold benzene or chloroform, less readily in ether. In contradistinction to the corresponding cotarnine compound, the hydrochloride is readily soluble in water; the dilute solution shows faint, bluish-green fluorescence. The aurichloride is an amorphous, light brown precipitate, soluble in hot alcohol, but separates in an oily condition on cooling.

An orange-yellow *picrate* separates in prismatic needles, melting at 173—174° on mixing hot alcoholic solutions of the base and picric acid.

Anhydrohydrastinine-2:4-dinitrotoluene,

$$\begin{array}{l} CH_2{:}O_2{:}C_6H_2\text{——}CH{\cdot}CH_2{\cdot}C_6H_3(NO_2)_2 \\ \qquad\quad | \qquad\qquad\quad | \\ \qquad\quad CH_2{\cdot}CH_2{\cdot}NMe \end{array}$$

Hydrastinine (2 grams) and 2:4-dinitrotoluene (2 grams) were dissolved in boiling methyl alcohol (30 c.c.), and the solution boiled until the yellow, granular precipitate began to separate. After cooling, the substance was collected and recrystallised from a mixture of benzene and methyl alcohol. The yield approximated closely to that demanded by theory.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1201 gave 0·2568 CO_2 and 0·0482 H_2O. C=58·3; H=4·4.

$C_{18}H_{17}O_6N_3$ requires C=58·2; H=4·6 per cent.

The substance crystallises in microscopic balls of needles, is pale yellow, and melts at 143—144° with vigorous decomposition at a slightly higher temperature. It is very sparingly soluble in hot or cold alcohol, but readily so in benzene.

The *hydrochloride* is sparingly soluble in cold water, and can be crystallised from hot dilute hydrochloric acid. It forms pale yellow prisms.

The *picrate* is best prepared by mixing a hot solution of the base in methyl ethyl ketone with a solution of picric acid in the same solvent. It forms pale yellow prisms, melting at 172—173°, and is very sparingly soluble in the usual solvents.

The decomposition of this substance on boiling with acetic acid is quite similar to that of anhydrocotarnine-2:4-dinitrotoluene. The almost colourless solution of the base in glacial acetic acid acquires a yellow colour on boiling, and on dilution with water, needles, melting at 68° and consisting of dinitrotoluene, separate from the solution. The filtrate from these exhibits a strong bluish-green fluorescence showing the presence of hydrastinine.

In conclusion, we desire to thank the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

THE UNIVERSITY,
MANCHESTER.

CCXLI.—*The Electrochemistry of Solutions in Acetone. Part I.*

By Alexander Roshdestwensky and William Cudmore McCullagh Lewis.

Whilst a considerable amount of attention has been directed to the electrochemical behaviour of methyl and ethyl alcohols, relatively few measurements are recorded in the case of solutions in acetone. The present paper contains the results of an investigation undertaken to supply to a certain extent this deficiency. The solutes employed were lithium nitrate and silver nitrate, the latter being examined in greater detail. Before giving our own measurements, it is necessary to indicate briefly some of the results obtained by other observers which bear directly on the results obtained by us.*

As regards the electrolysis of saturated silver nitrate solutions in acetone, Kahlenberg (*J. physical Chem.*, 1900, **4**, 349) found that the metal was precipitated in a coherent form, but "the solution conducts so poorly" that it was impossible to verify Faraday's law. In the same paper Kahlenberg gives some results of electromotive force measurements of $Ag|AgNO_3$ concentration cells in pyridine and acetonitrile respectively, with regard to which he concludes that the Nernst expressions are inapplicable. Kahlenberg assumes that the liquid/liquid potential difference is negligible, which, in the case of acetone at least, we shall show later is not the case.

The specific conductivity of acetone itself has been measured by Dutoit and Levier (*J. Chim. phys.*, 1905, **3**, 435), the value obtained being $(2-0{\cdot}48)\times 10^{-7}$ mho at the ordinary temperature (using unplatinised platinum electrodes). H. C. Jones and C. A. Rouiller (*Amer. Chem. J.*, 1906, **36**, 427) obtained the value $1{\cdot}0\times 10^{-6}$ at 0°, our own result being 6×10^{-7} at 18° (using unplatinised electrodes †).

As regards the molecular conductivity of solutes at infinite dilution (λ_∞) in acetone, considerable vagueness exists. Carrara (*loc. cit.*) states that λ_∞ for triethylsulphine iodide is 167 (as determined by direct experiment). Walden (*Zeitsch. physikal. Chem.*, 1906, **54**, 222) found for tetraethylammonium iodide at 25°

* For a general account of the electrochemistry of non-aqueous solutions, compare Carrara: "Elektrochemie der nichtwässrigen Lösungen," Ahrens' *Sammlung*, **12**; also Neustadt, *Diss.*, Breslau, 1909.

† These are preferable to platinised ones, as they eliminate the possibility of catalytic reactions when the solvent is an organic substance.

$\lambda_\infty = 225$. Dutoit and Levier (*loc. cit.*) give the following values for some simple salts at 18°:

	Li.	Na.	K.	NH_4.
Br	155	158	155·5	157·5
I	157	155	157·5	157·5
CNS	—	169	170·0	171·0
NO_3*............	132	—	—	—

* Benz, *Diss.*, Lausanne, 1905.

From these results Dutoit and Levier conclude that Kohlrausch's law of the independent migration of the ions is valid for solutions in acetone. The same authors have applied Ostwald's dilution law to some of the above salts, but find that the "constant" falls with increasing dilution.

In connexion with the question of transport numbers, Carrara (*loc. cit.*) draws the conclusion that in general there is a tendency on the part of each ion to reach a limiting value independent of the nature of the solvent. This scarcely seems to be borne out in the case of acetone, however. In the particular instance of silver nitrate, Jones and Rouiller (*loc. cit.*) state that the solubility of the salt in acetone is too slight to make a direct determination of the transport number, but that a value may be obtained by extrapolation from results obtained in acetone–water mixtures, the acetone concentration rising from zero to 75 per cent. Naturally, the extrapolation is a rather large one, and Jones and Rouiller have only felt justified in giving the result as an inequality, namely, the transport number of NO_3' at 25° in acetone $> 0·62$.

Experiments with methyl alcohol–acetone mixtures also lead on extrapolation to a value for the transport number greater than 0·6.

Experimental.

Kahlbaum's acetone was twice distilled over metallic calcium, the middle fraction being kept in a glass bottle, from which moisture was carefully excluded by calcium chloride tubes.

The most concentrated solution of silver nitrate conveniently prepared was $0·02N$. The solvent and solutions were kept, and the measurements carried out in weak artificial light, as it was noticed that on exposure to sunlight a brown precipitate forms in the solutions. Under the conditions specified the solutions remain permanently homogeneous.

I.—*Conductivity Measurements.*

The usual Wheatstone bridge and telephone method was employed. The cell, from which moisture was excluded, contained

two large unplatinised platinum plates close together, the cell constant being small, namely, 0·09213.

The measurements were made at 18°, an oil-bath being employed as the resistances were in all cases fairly large. The following table contains the specific and molecular conductivities of silver nitrate.

TABLE I.

Concentration in gram-mols./litre.	Specific conductivity (mhos) × 10^5.	λ_v. Molecular conductivity.
0·02	14·37	7·19
0·01	10·17	10·17
0·007	7·42	10·60
0·005	5·50	11·00
0·0035	3·97	11·34
0·002	2·51	12·54
0·001	1·46	14·62
0·0005	0·98	19·68

Our values at 18° are slightly lower than those of Laszczynski, and slightly higher than those of Jones and Rouiller (at 25°).

The value of λ_∞ for silver nitrate cannot be obtained directly. The empirical expression $\lambda_\infty\,\eta=$constant (compare Walden, *Zeitsch. physikal. Chem.*, 1906, **55**, 207) independent of the solvent, η being the viscosity of the solvent, does not appear to hold for acetone; thus, on comparing the viscosities of water and acetone, one finds that λ_∞ for silver nitrate in acetone $=371$, a value which is certainly too great. Again, Kohlrausch's expression, $\lambda_v=\lambda_\infty - a\sqrt[3]{c}$, where a is a constant and c the concentration, has found application in those cases in which λ_v is a linear function of $\sqrt[3]{c}$; although this condition is approximately fulfilled in the present instance, the values for λ_∞ given by the formula vary from 45 to 78.

A moderate approximation may, however, be obtained in the following way: According to Laszczynski, λ_∞ for simple salts in acetone is 1·3 times that in water. For silver nitrate at 18°, $\lambda_\infty=116$, and hence in acetone $\lambda_\infty=151$. This is not very different from the directly determined values for alkali bromides and iodides in acetone ($\lambda_\infty=155$—160, Dutoit and Levier), and since in water the λ_∞ for silver nitrate does not differ much from that of these salts, we have assumed that the same holds for acetone solution and have taken λ_∞ for silver nitrate $=150$. The conclusions which we draw from the results in which λ_∞ is employed are not invalidated, even if a large percentage error (up to 30 per cent.) were involved in this quantity; further, the majority of the electromotive force measurements given later are independent of λ_∞.

The following table contains the degrees of dissociation of silver nitrate in acetone, the Ostwald dilution law $\alpha^2/(1-\alpha)v$, and the

empirical expressions $\alpha^3/(1-\alpha)^2 v$ and $\alpha^2/(1-\alpha)\sqrt{v}$ of van't Hoff and Rudolphi respectively.

TABLE II.

Molar concentration.	$\alpha=\lambda_v/\lambda_\infty$.	Ostwald K.	van't Hoff K.	Rudolphi K.
0·02	0·048	$0·0_4 48$	$0·0_5 244$	$0·0_3 342$
0·01	0·068	50	362	496
0·007	0·070	37	277	442
0·005	0·073	29	226	407
0·0035	0·075	21	173	360
0·002	0·084	15	141	345
0·001	0·097	14	102	329
0·0005	0·131	09	149	441

The Ostwald constant falls steadily as the dilution increases. The van't Hoff constant is also not very satisfactory, the most consistent values being given by Rudolphi's formula. It is thus apparent that silver nitrate in acetone behaves like a strong electrolyte in not obeying Ostwald's law, but at the same time the extent of the dissociation is that of a weak electrolyte (in water). This opens the question as to what is the criterion to be employed to decide whether an electrolyte is "weak" or "strong."

The conductivity of lithium nitrate in acetone (which is required in connexion with the *E.M.F.* measurements) was also determined, with the following result.

TABLE III.

Lithium Nitrate in Acetone at 18°.

Molar concentration.	Specific conc. $\times 10^3$.	λ_v.	$\alpha=\lambda_v/\lambda_\infty$.	Ostwald K.	Rudolphi K.
0·343*	2·4	7·0	0·053	$0·0_2 101$	$0·0_2 176$
0·1715	1·39	8·1	0·061	067	160
0·0858	0·82	9·54	0·072	048	—
0·0429	0·50	11·6	0·088	036	—
0·0214	0·31	14·5	0·110	029	$0·0_2 200$
0·0107	0·20	19·0	0·144	026	—
0·0053	0·13	24·5	0·186	022	—
0·0026	0·087	33·4	0·253	022	$0·0_2 430$
0·0013	0·057	44·0	0·333	022	—
0·00065	0·037	57·0	0·432	021	$0·0_2 840$
0·00032	0·024	75·0	0·568	023	0·0120

* Saturated.

The value of λ_∞ for lithium nitrate as determined by Benz (Dutoit and Levier, *loc. cit.*) is 132, and this has been employed in the calculation of the three last columns in the above table.* It will be observed that for dilutions $v > 100$ the Ostwald expression is constant, whilst the Rudolphi formula does not hold—and this

* Kohlrausch's formula is also inapplicable here, because λ is not a linear function of $\sqrt[3]{c}$.

in spite of the fact that the dissociation is much greater than in the case of silver nitrate. Dissociation of itself is therefore not necessarily the source of the inapplicability of the Ostwald law. From the data given above it is found that the concentration of NO_3' in the saturated solution of lithium nitrate is 0·0182 gram-ions per litre at 18°. This quantity is required later.

II.—*Electromotive Force Measurements.*

A calibrated slide-wire potentiometer (Land- und Seekabelwerke) accurate to 0·1 millivolt was employed. The Weston cell was taken as standard (*E.M.F.* = 1·0183 volts). Since it was anticipated that the quantity of current which could be obtained from the silver nitrate concentration cells would be very small, a galvanometer was not employed. Instead, an evacuated capillary electrometer was used. This type of instrument suffers as a rule from the defect that its capacity is too great. The vacuum type, however, is much more sensitive than the ordinary form, probably due to the fact that since air is excluded the quantity of Hg^{++} ions in solution is less than in the ordinary instrument, and hence the capacity of the Helmholtz double-layers is less.* Employing the Weston cell as a source of *E.M.F.*, it was observed that with the electrometer readings could be made to 0·1 millivolt. With the silver nitrate-acetone cells the reading is only accurate to 2 millivolts. The sensitivity is therefore not sufficient for very accurate work.

Electromotive Forces which include Liquid/Liquid Potential Difference.

For the ordinary type of cell,

$$\mathrm{Ag} \left| \begin{array}{c} \mathrm{AgNO_3} \\ c_1. \end{array} \right| \begin{array}{c} \mathrm{AgNO_3} \\ c_2. \end{array} \left| \mathrm{Ag}, \right.$$

the expression for the electromotive force at 18° is:

$$E = \frac{2v}{u+v}\frac{RT}{nF}\log\frac{\alpha_1 c_1}{\alpha_2 c_2} \text{ or } \frac{2v}{u+v}\ 0{\cdot}0577 \log\frac{\lambda_1 c_1}{\lambda_2 c_2}.$$

where λ_1, λ_2 are the molecular conductivities at the $AgNO_3$ concentrations c_1 and c_2; $v/u+v$ = transport number of NO_3' = 0·62.

It was our object to investigate if the Nernst formula held good for acetone solutions. Table IV contains the results obtained, the headings of the columns being self-explanatory.

It will be observed that the differences between observed and calculated values are about as frequently positive as negative. The results obtained therefore support the view that Nernst's formula is applicable. Incidentally, also, the agreement obtained goes to show

* Experiments are being undertaken in this laboratory with a view further to improve, if possible, the sensitivity of the capillary electrometer.

Table IV.

Temperature.	Molar concentration of $AgNO_3$. c_1.	c_2.	*E.M.F.* observed 1st determination.	2nd.	3rd.	*E.M.F.* calculated.
19°	0·02	: 0·01	0·014	0·013	{0·015, 0·013}	0·011
19·5	0·02	: 0·007		0·020	0·020	0·028
19	0·02	: 0·005	[0·029]	0·034	0·035	0·033
20	0·02	: 0·0035		0·045	0·045	0·040
19	0·02	: 0·002	0·054	0·052	0·052	0·054
19	0·02	: 0·001	0·056	0·057	0·058	0·070
19	0·02	: 0·0005	{0·085, 0·086}	0·084	0·085	0·087
20	0·02	: 0·00005		0·121	0·121	—
19	0·01	: 0·007		0·012	0·011	0·009
19	0·01	: 0·005		0·025	0·024	0·019
20	0·01	: 0·0035		0·029	{0·028, 0·027}	0·026
19	0·01	: 0·002		0·037	0·038	0·043
19	0·01	: 0·001		0·045	0·045	0·060
19	0·01	: 0·0005		0·074	0·073	0·073
19	0·01	: 0·00005	0·119	0·120	0·118	—
20	0·007	: 0·005		0·013	0·015	0·009
20	0·007	: 0·0035		0·015	{0·017 *, 0·016}	0·019
20	0·007	: 0·002		0·032	0·032	0·033
20	0·007	: 0·001		0·042	0·042	0·050
20	0·007	: 0·0005		{0·055, 0·056}		0·062

* Neustadt measured this combination, his value being 0·016—0·017*v*, which is in good agreement with our result. Neustadt did not attempt to calculate the *E.M.F.*

that the value 0·62 for the transport number of NO_3' in acetone must be fairly correct. Employing this, we can calculate the magnitude of the liquid/liquid potential differences (included in the above measurements) by means of the expression:

$$E_1 = \frac{u-v}{u+v}\ 0{\cdot}0577 \log\frac{\lambda_1 c_1}{\lambda_2 c_2}.$$

Table V.

Liquid/Liquid Potential Difference in Volts (at 18°).

Molar concentration of $AgNO_3$.	P.D. calculated.
0·02 : 0·01	0·002
0·02 : 0·001	0·013
0·01 : 0·007	0·001
0·01 : 0·005	0·004
0·01 : 0·002	0·008
0·01 : 0·001	0·012
0·01 : 0·0005	0·014

The liquid/liquid potential difference is therefore not negligible when the concentration-ratio of the salt exceeds 5.

Attempts to Eliminate the Liquid/Liquid Potential Difference.

As ammonium nitrate has been frequently employed in aqueous solution to eliminate the liquid potential difference, we had hoped to employ it in the present case, but its solubility in acetone is very slight, as is also the solubility of sodium nitrate. Ammonium acetate dissolves to a certain extent, but it is unsuitable for the purpose, since the solution (in presence of air) darkens, and on pouring it into water a green fluorescence is observed, indicating the formation of a compound. The solubility of potassium nitrate in acetone at 18° was found to be 0·001 gram-molecule per litre. A saturated solution of dry lithium nitrate was under the same conditions found to be 0·343*N*. Owing to its greater solubility, lithium nitrate was therefore employed, although the great inequality in the mobility of its ions in water is not a recommendation.* Two sets of experiments were carried out, (*a*) with lithium nitrate (or potassium nitrate) interposed between the silver nitrate solutions, and (*b*) with lithium nitrate present throughout the cell.

(*a*) *Potassium and Lithium Nitrates Interposed.*

The following table contains the *E.M.F.* values obtained with potassium nitrate as the middle liquid:

TABLE VI.

Temperature.	Molar concentration of $AgNO_3$. c_1. : c_2.	*E.M.F* observed.	*E.M.F.* observed *without* KNO_3 interposed.
19°	0·01 : 0·007	0·011	0·011
19	0·01 : 0·005	0·024	0·024
20	0·01 : 0·0035	0·028	0·028
19	0·01 : 0·002	0·048	0·037
19	0·02 : 0·007	0·020	0·020
19	0·02 : 0·005	0·031	0·035
20	0·02 : 0·0035	0·045	0·045
19	0·02 : 0·002	0·053	0·052
19	0·02 : 0·001	0·058	0·058

The interposition of potassium nitrate has no reasonable effect, as was to be expected from its slight solubility. The measurements in this case were the most difficult to obtain.

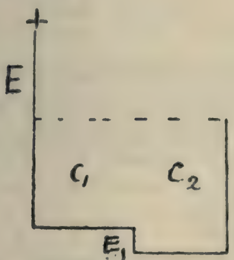
The following table contains the results obtained on interposing saturated lithium nitrate solution (0·343*N*) as the middle liquid:

* This is probably of little significance, however, since the Li ion has been shown to be greatly hydrated in aqueous solution, while it may be "normal" in acetone.

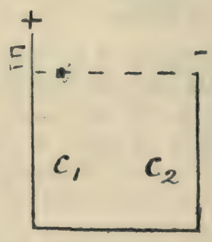
TABLE VII.

Temperature.	Molar concentration of $AgNO_3$. c_1 : c_2.	*E.M.F.* observed.	*Increase* in *E.M.F.* in volts due to interposition of $LiNO_3$.
19°	0·02 : 0·01	0·019, 0·020	0·005
19	0·02 : 0·007	0·028	8
19	0·02 : 0·005	0·041	7
19	0·02 : 0·0035	0·052	7
19	0·02 : 0·002	0·068	16
19	0·02 : 0·001	0·065	7
19	0·02 : 0·0005	0·134 (?)	47 (?)
19	0·01 : 0·007	0·017, 0·019	6
19	0·01 : 0·005	0·034	9
19	0·01 : 0·0035	0·035	8
20	0·01 : 0·002	0·064	7
19	0·01 : 0·001	0·053	8
20	0·01 : 0·0005	0·075	2
20	0·007 : 0·005	0·022	8
20	0·007 : 0·0035	0·023	7
20	0·007 : 0·002	0·038, 0·039	6
20	0·007 : 0·001	0·048	6
20	0·007 : 0·0005	0·063	7

The important fact brought out by the above results is that a saturated solution of lithium nitrate *raises* the *E.M.F.* of the cell instead of lowering it, as one would expect in accordance with the following:



$c_1 > c_2$. Liquid/liquid P.D. $= E_1$.
Transport number of anion $> 0·5$.
Net *E.M.F.* of cell $= E$.



$E_1 = 0$.
Net E should be less than in previous case.

The lithium nitrate solution, instead of eliminating E_1, sets up a potential difference of its own in the same sense as the E_1 in the original case.

(b) Lithium Nitrate Solution Throughout the Cell.

In view of the abnormal behaviour of lithium nitrate when interposed, it is of interest to examine its effect when distributed throughout the cell, in which case, on theoretical grounds, any convenient electrolyte sufficiently soluble should eliminate the liquid/liquid potential difference. First, it is necessary to tabulate the

values for the silver ion concentration in the various solutions when allowance is made for the presence of the saturated lithium nitrate solution. As we have already seen, this solution gives rise to a NO_3' concentration 0·0182 gram-ions per litre, which may be regarded as remaining practically constant in all cases, thereby throwing back the dissociation of the silver nitrate to a different extent in each solution. The problem would be easy if silver nitrate in acetone obeyed the dilution law, but this is not the case. As an approximation, however, the silver ion concentration in presence of the lithium salt has been calculated, first, by employing the various values found for the Ostwald "constant" at the corresponding molar concentrations of the silver salt, the results being given in the following table, column 2; and, secondly, by employing the mean of the values of the Ostwald constant, the results in this case being given in the third column.

TABLE VIII.

Molar concentration of $AgNO_3$.	$[Ag^{\cdot}]$ calculated from the corresponding "K."	$[Ag^{\cdot}]$ calculated from the mean $K = 0{\cdot}0_428$.
0·02	$0{\cdot}0_4527$	$0{\cdot}0_4307$
0·01	$0{\cdot}0_4275$	$0{\cdot}0_4154$
0·007	$0{\cdot}0_4142$	$0{\cdot}0_4107$
0·005	$0{\cdot}0_579$	$0{\cdot}0_577$
0·002	$0{\cdot}0_516$	$0{\cdot}0_538$
0·001	$0{\cdot}0_677$	$0{\cdot}0_515$
0·0005	$0{\cdot}0_625$	$0{\cdot}0_677$

The values of the silver ion concentration thus obtained are used to calculate the *E.M.F.* of the cell (containing lithium nitrate throughout), the formula when there is no liquid/liquid potential difference being:

$$E = 0{\cdot}0577 \log \frac{[Ag^{\cdot}]_{I}}{[Ag^{\cdot}]_{II}},$$

in which the square brackets denote concentration terms. In the following table are given the observed *E.M.F.*'s, the *E.M.F.* calculated from the data in column 2, table VIII, and the *E.M.F.*'s calculated from column 3, table VIII, respectively.

TABLE IX.

Temperature 19°.

Molar concentrations of $AgNO_3$.	*E.M.F.* in volts observed.	*E.M.F.* calculated from col. 2, table VIII.	*E.M.F.* calculated from col. 3, table VIII.
0·02 : 0·01	0·013	0·0163	0·0173
0·01 : 0·007	0·0122	0·0166	0·009
0·01 : 0·005	0·0245, 0·0249	0·0313	0·0173
0·01 : 0·002	0·060	0·0715	0·035
0·01 : 0·001	0·069	0·0895	0·0583
0·01 : 0·0005	0·086	0·118	0·0750

It may be noted that with lithium nitrate throughout the cell measurements could be made much more easily than in the previous cases. The error does not exceed 0·5 millivolt.

We may also obtain a series of values by calculation, without taking the silver ion concentration values into account, if we assume that the dissociation of silver nitrate approximately obeys the dilution law, and that the dissociation is small compared to that of lithium nitrate. In such a case we have:

$$\frac{[Ag^{\cdot}]_{I}}{[Ag^{\cdot}]_{II}} = \frac{\text{Molar concentration } AgNO_{3I}}{\text{Molar concentration } AgNO_{3II}}.$$

The values worked out by this method were practically identical with those given in column 4, table IX.

It will be observed that the found values lie between the two series of calculated values. It is therefore impossible to state with certainty whether there is agreement or not, the indefiniteness arising from the fact that silver nitrate does not obey Ostwald's dilution law accurately.

Summary.

(1) Silver nitrate in acetone is only slightly dissociated. It does not, however, obey Ostwald's dilution law, but gives a good constant in Rudolphi's expression.

(2) Lithium nitrate in acetone is much more dissociated than silver nitrate. For dilutions $v > 100$ Ostwald's law holds well. Rudolphi's expression does not hold.

(3) It has been shown that the electromotive force of the silver nitrate concentration cell in acetone at 19°, arranged so as to contain a liquid/liquid potential difference as well as electrode potential differences, is in quantitative agreement with Nernst's formula, the value of the transport number of NO_3' being taken as 0·62.

(4) The interposition of a saturated solution of lithium nitrate between the two silver nitrate solutions, instead of eliminating the liquid/liquid potential difference, increases the latter by several millivolts. The introduction of lithium nitrate throughout the cell has the desired effect so far as it has been possible to decide in view of the approximate nature of our knowledge of the silver ion concentration.

In conclusion, we wish to thank Dr. N. T. M. Wilsmore for the interest which he has taken in these experiments.

Physical Chemistry Laboratory,
University College, London.

CCXLII.—*Chemical Examination of Calabar Beans.*

By Arthur Henry Salway.

The so-called Calabar beans, the ripe seed of *Physostigma venenosum*, Balfour, have previously been the subject of several investigations, and their most important constituent—the alkaloid physostigmine or eserine—has long been recognised by most of the national Pharmacopœias on account of its valuable medicinal properties.

The first chemical examination of Calabar beans was conducted by Jobst and Hesse (*Annalen*, 1864, **129**, 115), who ascertained that their poisonous action is due to an alkaloid, which they designated physostigmine. This substance was obtained by them only as an amorphous, varnish-like mass, but a year later Vée (*Jahresber.*, 1865, 456) succeeded in isolating the alkaloid in a crystalline state. The last-mentioned investigator found that the alkaloid melted at 69°, and proposed for the crystalline base the name eserine. Jobst and Hesse, in a later investigation (*Annalen*, 1867, **141**, 913), assigned to physostigmine the formula $C_{15}H_{21}O_2N_3$, but still expressed doubt regarding its crystalline character, although it is now known that under suitable conditions the alkaloid, as stated by Vée (*loc. cit.*), can be obtained in the crystalline form.

In the year 1876 Harnack and Witkowski (*Arch. experim. Path.*, 1876, 401) indicated the presence of a second alkaloid in Calabar beans, for which they proposed the name calabarine. This substance was very indefinite in character, being chiefly distinguished by its tetanus-like effects on the living organism. Subsequent investigations, notably that of Ehrenberg (*Verh. Ges. Deut. Naturf. Aertzte*, 1893, II, 102), have shown that calabarine was in all probability a product of decomposition, and could not have pre-existed in the Calabar bean. It is evident, however, that besides physostigmine a very small proportion of other alkaloids is contained in the Calabar bean; thus, in the year 1888, a crystalline base, differing from physostigmine, was obtained by Böhringer & Söhne (*Pharm. Post*, 1888, **21**, 663), and termed by them eseridine. This base was stated to melt at 132°, to be much less poisonous than physostigmine, and on heating with dilute mineral acids to become converted into the latter alkaloid. Eseridine has been further examined by Eber (*Pharm. Zeit.*, 1892, **37**, 483), who assigned to it the formula $C_{15}H_{23}O_3N_3$, and it is thus seen to differ from physostigmine only in the elements of one molecule of water.

Ehrenberg (*loc. cit.*) succeeded in isolating a third alkaloid from the Calabar bean. This substance, which is present in extremely

small proportions, was named eseramine, and the empirical formula $C_{16}H_{25}O_3N_4$ assigned to it. It was described as a substance very sparingly soluble in ether and melting at 238—240°. Still another alkaloid of Calabar bean has more recently been described by Ogui (*Apoth. Zeit.*, 1904, **19**, 891). This base is stated to be isomeric with physostigmine, and therefore designated *iso*physostigmine. The only information concerning it appears to be the fact that it is insoluble in ether, and yields a sulphate melting at 200—202°.

Little is known regarding the constitution of physostigmine, and practically nothing of the alkaloids associated with it. It therefore seemed desirable to undertake some experiments for the purpose of throwing further light on the chemical constitution of these bases. To achieve this object a large quantity of Calabar beans was obtained and worked up for the isolation of the alkaloids. At the same time, the opportunity was taken to examine more completely the other constituents of the bean. The experiments undertaken in order to elucidate the constitution of physostigmine are reserved for a future communication.

Experimental.

A representative sample of the Calabar beans employed in this investigation, when assayed by the method of the United States Pharmacopœia, yielded 0·091 per cent. of alkaloid. The method referred to, however, was found to give results which were much too low, since the amount of physostigmine isolated when working on the large scale, as described below, was equivalent to 0·179 per cent. of the material employed. The low result by the above method of assay has been ascertained to be due to the fact that three extractions with ether (as required by the Pharmacopœia) are quite insufficient to remove the alkaloid completely from a solution which has been rendered alkaline with sodium hydrogen carbonate.

With the object of testing for the presence of an enzyme, 500 grams of powdered material were mixed with water and kept at the ordinary temperature for forty-eight hours. The liquid was then separated from the mass by filtration under pressure, and alcohol added to the filtrate. A caseous, white precipitate was thus produced, which was collected and dried in a vacuum desiccator over sulphuric acid, when it amounted to 14·5 grams. This substance, which gave the biuret reaction, slowly hydrolysed amygdalin, thus indicating the presence of an enzyme.

A further portion (50 grams) of the powdered bean was successively extracted in a Soxhlet apparatus with various solvents, when

the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°)	extracted	0·38	grams	= 0·76	per cent.
Ether	,,	0·08	,,	= 0·16	,,
Chloroform	,,	0·18	,,	= 0·36	,,
Ethyl acetate	,,	0·13	,,	= 0·26	,,
Alcohol	,,	2·32	,,	= 4·64	,,
	Total.........	3·09	,,	6·18	,,

For the purpose of a complete examination of the constituents of the bean 122·7 kilograms of finely powdered material were extracted by continuous percolation with hot alcohol. After removal of the greater part of the alcohol there remained a reddish-brown extract, amounting to 10½ kilograms. This extract, in convenient portions, was mixed with water, and the mixture distilled in a current of steam. The distillate, which contained a very small quantity of essential oil, was extracted with ether, the ethereal solution being washed, dried, and the ether removed. A pale yellow oil possessing a garlic-like odour and amounting to 1·5 grams was obtained.

After the above operation there remained in the steam distillation flask a large quantity of fatty oil floating on the surface of a reddish-brown aqueous liquid, which contained a brown, resinous powder in suspension. The fatty oil was separated, washed well with water, and set aside for subsequent examination, whilst the brown resin was collected and washed with water, the washings being added to the main portion of the aqueous liquid.

Isolation of Physostigmine, $C_{15}H_{21}O_2N_3$.

A small portion of the aqueous liquid was, in the first place, extracted successively with ether and amyl alcohol, but these solvents removed only small quantities of gummy material. The whole of the aqueous liquid was then rendered alkaline with an excess of sodium carbonate, and repeatedly extracted with ether until no further alkaloidal substance was removed by this treatment. The ethereal extracts were united, concentrated to a convenient volume, and then carefully shaken with successive portions of 5 per cent. sulphuric acid until the extract became just acid in reaction. The neutral solution of the sulphate of the alkaloid was then treated with an excess of a saturated solution of sodium salicylate, when the salicylate of the alkaloid was precipitated as an almost colourless, crystalline powder. This was collected, washed well with water, and dried in a vacuum desiccator over sulphuric acid. A further quantity of the salicylate of the alkaloid was obtained from the filtrate by rendering it alkaline with sodium carbonate, extract-

ing with ether, and subjecting the ethereal solution to the same process as that described above. The total crude salicylate thus obtained amounted to 330 grams, representing 219·7 grams of physostigmine, which is equivalent to 0·179 per cent. of the material employed in the investigation. In order to ascertain whether this crude salicylate was homogeneous or not, a considerable portion of the compound was subjected to systematic fractional crystallisation from alcohol. The fractions were found to be uniform in character, crystallising in stout, colourless prisms, melting at 180—181°, and were therefore homogeneous. (Found, C = 64·1; H = 6·6; N = 10·2. Calc., C = 63·9; H = 6·5; N = 10·2 per cent.)

It is evident that the above compound consisted of physostigmine salicylate. The free base was obtained from the latter by agitation with aqueous sodium carbonate in the presence of ether. The ethereal solution of physostigmine thus obtained was dried, and the solvent removed. The pale brown, viscid residue was dissolved in benzene, and the solution allowed to evaporate slowly at the ordinary temperature in a vacuum desiccator over sulphuric acid. After some time there was deposited a mass of crystals, which was collected and recrystallised several times from a mixture of benzene and petroleum. The physostigmine separated from this solvent in stout prisms, which melted at 86—87°. (Found, C = 65·1; H = 7·9. Calc., C = 65·5; H = 7·6 per cent.)

0·2659, made up to 20 c.c. with chloroform, gave α_D $-2°1'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-75·8°$.

The above specimen of physostigmine does not agree in melting point with the physostigmine obtained by Pictet and Polonowsky (*Bull Soc., chim.*, 1893, [iii], **9**, 1008), who state that the alkaloid melts at 105—106°. A commercial sample of physostigmine was therefore procured, and this also melted at 105—106°. It was then found that the alkaloid is dimorphous, since the modification melting at 86—87° could be readily converted into the substance melting at 105—106° by recrystallisation in the presence of a crystal of the latter. The optical rotation of the compound melting at 105—106° was determined, and found to be identical with that of the modification melting at 86—87°, as recorded above:

0·3062, made up to 20 c.c. with chloroform, gave α_D $-2°19'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-75·8°$.

Pictet and Polonowsky (*loc. cit.*) ascribe to physostigmine an optical rotation, $[\alpha]_D$ $-82°$, which is somewhat higher than the results obtained above.

Physostigmine does not yield any definite aurichloride or platinochloride, but a well-defined *picrate* was obtained, which crystallises

from dilute alcohol in feathery, yellow needles, melting at 114°. It is only sparingly soluble in hot water, but readily so in alcohol.

Isolation of Eseramine.

The ethereal liquid which had been shaken with dilute sulphuric acid for the separation of the physostigmine as above described was washed with water, dried, and the solvent removed. A small amount (about 2 grams) of a viscid, brown residue was thus obtained, which gradually became solid. Since the solid was not completely soluble in ether, it was digested with a small quantity of the latter, the sparingly soluble portion collected, and then purified by crystallisation from alcohol, when it separated in small, colourless needles, melting and decomposing at 245°. This substance was very sparingly soluble in ether, chloroform, or benzene, but readily so in hot alcohol. It dissolved in strong mineral acids, and yielded a precipitate with Mayer's reagent. It appears from the above properties that the substance is identical with the eseramine of Ehrenberg (*loc. cit.*), but the amount isolated (0·1 gram) did not admit of further examination.

Isolation of a New Alkaloid, Physovenine, $C_{14}H_{18}O_3N_2$.

The ethereal liquid from which the above-mentioned eseramine had been removed, yielded on evaporation a brown, oily residue, which slowly crystallised. The crystals were separated from a little adhering oil, and then crystallised, first from dilute alcohol, and finally from a mixture of benzene and light petroleum. The substance separated from the latter solvent in small, colourless prisms, melting at 123°. The yield of pure substance amounted to 0·6 gram:

0·1024 gave 0·2395 CO_2 and 0·0669 H_2O. C = 63·8; H = 7·3.
0·1165 „ 0·2726 CO_2 „ 0·0736 H_2O. C = 63·8; H = 7·0.
0·1817 „ 17·2 c.c. N_2 (moist) at 25° and 764 mm. N = 10·6.
$C_{14}H_{18}O_3N_2$ requires C = 64·1; H = 6·9; N = 10·7 per cent.

The above-described alkaloid is not identical with any of the bases previously isolated from Calabar beans, and since no compound of the formula $C_{14}H_{18}O_3N_2$ appears to have been hitherto described, it is proposed to designate the new alkaloid, *physovenine.*

Physovenine, $C_{14}H_{18}O_3N_2$, is very soluble in alcohol, benzene, or chloroform, moderately so in ether, but insoluble in light petroleum or water. It is only a weak base, dissolving in concentrated mineral acids, but being reprecipitated on the addition of water. When physovenine is treated with barium hydroxide, there is an immediate precipitation of barium carbonate, and the solution rapidly

assumes a deep red colour. This behaviour of physovenine is very similar to that of physostigmine, since the latter under the influence of alkalis (Ehrenberg, *loc. cit.*) loses carbon dioxide and methylamine, and becomes converted successively into eseroline and a red colouring matter, rubreserine. It appears probable from the properties and composition of physovenine that the latter is an intermediate product in the conversion of physostigmine into eseroline, as represented by the following equations:

$$\underset{\text{Physostigmine.}}{C_{15}H_{21}O_2N_3} + H_2O = \underset{\text{Physovenine.}}{C_{14}H_{18}O_3N_2} + CH_3{\cdot}NH_2.$$

$$C_{14}H_{18}O_3N_2 = \underset{\text{Eseroline.}}{C_{13}H_{18}ON_2} + CO_2.$$

Physovenine is, like physostigmine, very powerfully myotic; thus a single drop of a 0·1 per cent. solution of the alkaloid in dilute alcohol when introduced into the eye produced after an interval of a few minutes a powerful contraction of the pupil, which attained its maximum effect half an hour after the injection.

A portion of the aqueous liquid from which the alkaloids had been extracted as described above, was rendered slightly acid with acetic acid, and then concentrated to a small bulk. A large amount of a viscid syrup was thus obtained, which readily reduced Fehling's solution. It was digested with hot alcohol, the alcoholic liquid decanted, and ethyl acetate added to the latter. In this manner a considerable quantity of a sugar was obtained, which yielded a glucosazone, melting and decomposing at 205°.

The Fatty Oil.

The fatty oil which had been isolated as previously described amounted to 1650 grams. Since it was found to contain a small quantity of alkaloidal substance of weakly basic character, it was extracted with 40 per cent. sulphuric acid. The acid extracts were rendered alkaline and extracted with ether. In this manner a small amount (1·5 grams) of a brown, viscid liquid was obtained, which partly solidified after keeping some time. On examination, the crystalline substance was found to be identical with the alkaloid physovenine, $C_{14}H_{18}O_3N_2$, previously isolated from the aqueous liquid.

A convenient portion (200 grams) of the fatty oil was next hydrolysed by heating with an excess of potassium hydroxide in the presence of alcohol, when a considerable quantity of ammoniacal vapours was evolved. After this treatment the greater part of the alcohol was removed, water added, and the alkaline liquid repeatedly

extracted with ether. The pale yellow ethereal extract was washed, dried, and the ether removed, when 10 grams of a crystalline residue were obtained. This was dissolved in hot alcohol, from which it separated in colourless leaflets, melting at 132—133°. This substance gave the colour reactions of the phytosterols, and evidently belonged to that class of compounds. Windaus and Hauth (*Ber.*, 1906, **39**, 4378; 1907, **40**, 3681) have already shown that the phytosterol of Calabar bean is a mixture of two compounds, namely, stigmasterol, $C_{30}H_{48}O$, and sitosterol, $C_{27}H_{46}O$, which were separated by them after conversion into the bromoacetyl derivatives. In order to ascertain whether the above crude phytosterol, melting at 132—133°, consisted of such a mixture, the substance was acetylated, and the acetyl derivative treated with bromine in the presence of acetic acid. The sparingly soluble bromo-derivative which separated was purified by crystallisation from a mixture of chloroform and alcohol, and was obtained in colourless leaflets, melting and decomposing at 205—206°. (Found, Br = 40·6. Calc., Br = 40·7 per cent.) This substance is evidently identical with the tetrabromoacetylstigmasterol described by Windaus and Hauth (*loc. cit.*). When debrominated by means of zinc dust the above compound yielded acetylstigmasterol (m. p. 140°), and the latter on hydrolysis was converted into stigmasterol, melting at 169°.

The mother liquors from the bromination, treated in the same manner, yielded successively acetylsitosterol (m. p. 128°) and sitosterol, $C_{27}H_{46}O$, melting at 134—135°. (Found, C = 83·7; H = 12·1. Calc., C = 83·9; H = 11·9 per cent.) It is thus evident that the above crude phytosterol, melting at 132—133°, consists of a mixture of stigmasterol and sitosterol.

Isolation of Trifolianol, $C_{21}H_{34}O_2(OH)_2$.

The alkaline aqueous liquid from which the above-described crude phytosterol had been extracted by ether was acidified with dilute sulphuric acid, when a dark-coloured, semi-solid precipitate of fatty acids was produced. A portion of the precipitate was observed to be sparingly soluble in ether, and this was therefore separately collected, when it formed a dark-coloured solid amounting to 5 grams. This sparingly soluble substance was first digested with hot alcohol, which removed the greater part of the colouring matter, and then treated with boiling chloroform. The latter solvent extracted a small amount of a colourless solid, which was purified by crystallisation from dilute pyridine, when it separated in microscopic needles, melting and decomposing at 295°. When dissolved in chloroform and acetic anhydride and a drop of concentrated sulphuric acid

added, it gave a transient pink coloration, changing to blue, and then to green. (Found, C = 71·4; H = 10·2. Calc., C = 71·6; H = 10·2 per cent.)

The properties of the above compound, together with the result of its analysis, indicate that the substance is identical with trifolianol, $C_{21}H_{34}O_2(OH)_2$, which was first isolated from red clover flowers (Power and Salway, Trans., 1910, **97**, 249). Its identity was confirmed by the formation of diacetyltrifolianol, which crystallised in flat, colourless needles, melting at 165—166°. (Found, C = 68·9; H = 9·2. Calc., C = 68·8; H = 9·2 per cent.):

0·2118, made up to 20 c.c. with chloroform, gave α_D $-0°31'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-24·4°$.

Isolation of a New Dihydric Alcohol, Calabarol, $C_{23}H_{34}O_2(OH)_2$.

The sparingly soluble substance which had been digested with chloroform for the removal of the trifolianol, as above described, was crystallised from dilute pyridine, when it separated in minute crystals, melting and decomposing at 290—300°. It was found, however, that this substance still contained a considerable proportion of trifolianol. A separation was effected by converting the substance into its benzoyl derivative and subjecting the latter to a systematic fractional crystallisation from a mixture of chloroform and alcohol. In this manner two benzoyl compounds were isolated, melting at 165—170° and 195—196° respectively. The former was found on analysis to be *dibenzoyltrifolianol*:

0·1109 gave 0·3052 CO_2 and 0·0822 H_2O. C = 75·1; H = 8·2.
$C_{35}H_{44}O_6$ requires C = 75·0; H = 7·9 per cent.

The benzoyl derivative melting at 195—196° was analysed with the following results:

0·1173 gave 0·3268 CO_2 and 0·0810 H_2O. C = 76·0; H = 7·7.
0·1088 „ 0·3036 CO_2 „ 0·0768 H_2O. C = 76·1; H = 7·8.
$C_{37}H_{44}O_6$ requires C = 76·0; H = 7·5 per cent.

0·5894, made up to 20 c.c. with chloroform, gave α_D $+0°52'$ in a 2-dcm. tube, whence $[\alpha]_D$ $+14·7°$.

It would appear from the above analysis that the benzoyl compound melting at 195—196° is derived from a dihydric alcohol, $C_{23}H_{36}O_4$. In order to isolate this compound in a state of purity a quantity of the original mixture of trifolianol and the new alcohol was heated with equal quantities of chloroform and alcohol, and the undissolved substance collected. On repeating the process several times a homogeneous compound was obtained, which melted at 245°. This was recrystallised from dilute pyridine, when it separated in colourless, microscopic needles:

0·0504 gave 0·1351 CO_2 and 0·0460 H_2O. C=73·1; H=10·1.

$C_{23}H_{36}O_4$ requires C=73·4; H=9·6 per cent.

The above substance is thus seen to possess the formula $C_{23}H_{36}O_4$. As it is a new compound it is proposed to designate it *calabarol*, with reference to the source from which it has been obtained.

Calabarol is very sparingly soluble in the usual organic solvents, but dissolves readily in pyridine. When dissolved in acetic anhydride and chloroform and a drop of concentrated sulphuric acid added, a pink coloration is produced, which rapidly changes to blue and then to green. Calabarol yields a *dibenzoyl* derivative, $C_{23}H_{34}O_4(CO{\cdot}C_6H_5)_2$, which crystallises from a mixture of chloroform and alcohol in well-formed, colourless needles, melting at 195—196°. It is readily soluble in ethyl acetate or chloroform, but very sparingly so in alcohol.

The properties of calabarol indicate that it is closely allied to a number of dihydric alcohols, which have been isolated in these laboratories, and which fall into two groups possessing the general formulæ $C_nH_{2n-6}O_4$ and $C_nH_{2n-8}O_4$ respectively. Calabarol, however, appears to belong to a new series of dihydric alcohols, which may be represented by the general formula $C_nH_{2n-10}O_4$.

Examination of the Fatty Acids.

The ethereal solution of fatty acids from which trifolianol and calabarol had been removed as described above, was washed, dried, and the ether removed. The residue was dissolved in hot alcohol, when a substance separated, which, after several crystallisations from alcohol, melted at 74—76°:

0·3073 required, for neutralisation, 8·85 c.c. $N/10$-KOH. Neutralisation value=161·5.

$C_{22}H_{44}O_2$ requires neutralisation value=165·0.

It appears from this result that the substance is behenic acid (m. p. 80—82°), although the melting point is somewhat low for the latter compound. In order, therefore, to effect a further purification, the substance was esterified, and the ethyl ester thus produced then distilled under diminished pressure. The first portion of the distillate having been discarded, the remainder was hydrolysed, when it yielded a fatty acid, melting at 77·5°. (Found, C=77·6; H=13·0. Calc., C=77·7; H=12·9 per cent.):

0·1775 required for neutralisation 5·2 c.c. $N/10$-KOH. Neutralisation value=164·3.

$C_{22}H_{44}O_2$ requires neutralisation value=165·0.

The substance was thus definitely identified as behenic acid

The remaining portion of the fatty acids was converted into the lead salt, and the latter treated with ether in the usual manner for the separation of the saturated from the unsaturated acids. The portion of lead salt insoluble in ether was collected, and the fatty acids regenerated and crystallised from alcohol. The first crystalline deposits consisted of behenic acid, melting at 77°. The subsequent deposits melted at about 55—60°, and were evidently mixtures. In order to ascertain the constituents of this product, it was dissolved in alcohol and fractionally precipitated by the successive addition of small portions of a concentrated solution of barium acetate. In this manner four fractions were obtained, from each of which the fatty acid was regenerated, then crystallised once from alcohol, and titrated with $N/10$-potassium hydroxide. The neutralisation values of the several fractions were 202·5, 205·9, 207·0, and 209·5, whilst their melting points were 55°, 59°, 59°, and 60° respectively. These results indicated the presence of palmitic and stearic acids.

The unsaturated acids obtained from that portion of the lead salt which was soluble in ether amounted to 80 grams. When distilled under diminished pressure a yellow oil which passed over at 215—240°/15 mm. was obtained. An analysis and a determination of the constants led to the following results:

0·1064 gave 0·3004 CO_2 and 0·1128 H_2O. C = 77·0; H = 11·8.
Neutralisation value = 199·6; Iodine value = 139.

$C_{18}H_{34}O_2$ requires C = 76·6; H = 12·1 per cent. Neutralisation value = 198·9; Iodine value = 90·1.

$C_{18}H_{32}O_2$ requires C = 77·1; H = 11·4 per cent. Neutralisation value = 200·4; Iodine value = 181·4.

It is thus evident that the liquid acids consisted of a mixture of oleic and linolic acids.

Examination of the Resins.

The resin which had been separated from the aqueous liquid in the manner previously described, consisted for the most part of a brown powder, which was very sparingly soluble in the usual organic solvents. This product was mixed intimately with purified sawdust, the mixture dried, and then extracted in a Soxhlet apparatus successively with petroleum, ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

This consisted of a brown, fatty oil, amounting to 65 grams. In order to ascertain whether the oil contained any alkaloid, it was dissolved in ether, and the ethereal solution shaken with dilute

sulphuric acid. The acid extracts yielded, however, only a very small quantity of a brown oil, which apparently consisted of physostigmine.

The ethereal solution which had been shaken with dilute sulphuric acid was washed, dried, and the solvent removed. The residue was then hydrolysed, and the products of hydrolysis examined in a manner similar to that previously described in connexion with the fatty oil of Calabar bean. The following constituents were found to be present: stigmasterol, sitosterol, trifolianol, calabarol, and behenic, palmitic, stearic, oleic, and linolic acids.

Ether, Chloroform, and Ethyl Acetate Extracts of the Resin.

These extracts were dark brown, gummy solids, amounting to 5, 17·5, and 11 grams respectively. They were separately examined, but nothing of a definite nature was isolated from them.

Alcoholic Extract of the Resin.

This was a dark brown syrup amounting to 41 grams. It was dissolved in alcohol, and the solution heated for some time with dilute sulphuric acid. After removal of the alcohol in a current of steam, there remained a black, resinous mass and a deeply coloured aqueous liquid. The former was collected and examined, but yielded nothing definite. Since a small portion of the aqueous liquid gave a precipitate with Mayer's reagent, the whole was rendered alkaline with sodium carbonate, and the alkaline mixture extracted repeatedly with ether. The ethereal extracts were united, and agitated with small portions of dilute sulphuric acid until the liquid was just acid in reaction. The extracts thus obtained when treated with a concentrated solution of sodium salicylate, yielded 3 grams of a crystalline solid, which was found to be identical with physostigmine salicylate, melting at 180—181°.

The alkaloid isolated as above described could not have existed as such in the alcohol extract of the resin, but was evidently present in some form of combination.

Summary.

The results of this investigation have shown that the Calabar bean (*Physostigma venenosum*, Balfour) contains, in addition to some essential oil, resin, and other amorphous substances, the following compounds:

Physostigmine, $C_{15}H_{21}O_2N_3$.—This alkaloid was found to be dimorphous, since two interconvertible modifications were obtained, melting at 86—87° and 105—106° respectively. The amount of

alkaloid isolated was equivalent to 0·179 per cent. of the Calabar beans employed.

Physovenine, $C_{14}H_{18}O_3N_2$, a new alkaloid, melting at 123°. Like physostigmine, it produces a powerful myotic effect on the pupil of the eye.

Eseramine, an alkaloid melting at 245°.

Calabarol, $C_{23}H_{36}O_4$, a new dihydric alcohol (m. p. 245°), which yields a *dibenzoyl* derivative, melting at 195—196°.

Trifolianol, $C_{21}H_{36}O_4$, a dihydric alcohol previously isolated from red clover flowers.

Stigmasterol, $C_{30}H_{48}O$, and sitosterol, $C_{27}H_{46}O$.

Glycerides of behenic, stearic, palmitic, oleic, and linolic acids.

A sugar yielding *d*-phenylglucosazone (m. p. 205°).

In the course of the present investigation no evidence has been obtained of the presence in Calabar beans of the alkaloid designated by Ogui (*loc. cit.*) as "*iso*physostigmine," or of the "eseridine" of Böhringer & Söhne (*loc. cit.*).

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CCXLIII.—*Contributions to the Chemistry of the Terpenes. Part XII. Synthesis of a Menthadiene from Thymol, and of a Diethyl*cyclo*hexadiene from Phenol.*

By GEORGE GERALD HENDERSON and ROBERT BOYD, B.Sc., Carnegie Research Scholar.

Preparation of a Menthadiene from Thymol.

THYMOMENTHOL (hexahydrothymol), $C_{10}H_{19}\cdot OH$, was first prepared synthetically by Brunel (*Compt. rend.*, 1905, **140**, 252) according to the method of Sabatier and Senderens, namely, by passing a mixture of thymol vapour and hydrogen through a tube containing finely divided nickel at a temperature of 160—170°. When heated with either potassium hydrogen sulphate or phosphoric oxide this thymomenthol yielded a menthene, $C_{10}H_{18}$, but as these dehydrating agents tend to bring about intramolecular rearrangements, the constitution of the hydrocarbon obtained by these methods remained uncertain. As we proposed to make use of this menthene for the preparation of a menthadiene, it appeared advisable to attempt to

dehydrate the thymomenthol by means of oxalic acid in order to obviate the risk of rearrangement. This reagent proved effective under suitable conditions.

A quantity of thymomenthol was prepared according to Brunel's method, and some of the product, which is a colourless liquid with a pleasant odour resembling that of mint, was boiled for a considerable time under a reflux condenser with an 8 per cent. aqueous solution of oxalic acid. The result was not satisfactory, little or no change taking place, and the use of stronger solutions led to no improvement. Finally, in order to effect dehydration, it was found necessary to heat the thymomenthol with anhydrous oxalic acid for several days. When the reaction appeared to be completed, the contents of the flask were distilled in a current of steam, with the result that a colourless, oily liquid passed over, whilst a smaller quantity of a non-volatile substance remained in the flask. The liquid distillate was separated from the condensed water, dried with potassium hydroxide, and fractionally distilled. The fraction which boiled at 166—170° was retained, and the portion of higher boiling point again heated with oxalic acid. Ultimately, after further fractionation, we obtained a quantity of a clear, colourless liquid with a pleasant odour, which had the following constants: boiling point 167—169° under atmospheric pressure, D_{20}^{20} 0·8188, n_D 1·45363. The physical properties of this menthene agree with those of Brunel's preparation, and it is therefore evident that when thymomenthol is dehydrated by means of oxalic acid the product is the same as that obtained by using either potassium hydrogen sulphate or phosphoric oxide.

According to its method of formation from thymomenthol (I), the hydrocarbon must be either Δ^2- (II) or Δ^3-menthene (III). We found that it yields the characteristic crystalline nitrosochloride, melting at 133°, and is therefore the Δ^3-isomeride:

$$\begin{array}{ccc}
\begin{array}{l} CH_2\text{-}CHMe\text{-}CH_2 \\ CH_2\cdot CHPr^{\beta}\ CH\cdot OH \end{array} &
\begin{array}{l} CH_2\text{-}CHMe\text{-}CH \\ CH_2\cdot CHPr^{\beta}\cdot CH \end{array} &
\begin{array}{l} CH_2\cdot CHMe\cdot CH_2 \\ CH_2\cdot CPr^{\beta}{=}CH \end{array} \\
\text{(I.)} & \text{(II.)} & \text{(III.)}
\end{array}$$

The other substance obtained by heating thymomenthol with anhydrous oxalic acid, which did not volatilise with steam, was proved to be *thymomenthyl oxalate*, $C_2O_4(C_{10}H_{19})_2$, which is formed as an intermediate product. This ester was separated from the other contents of the distillation flask by means of ether, the ethereal solution washed and dried, and the ether removed. On distillation of the residue a clear, colourless liquid passed over, which solidified on keeping. After crystallisation from alcohol the ester was obtained in large, colourless, lustrous prisms, which melted at 90°. It is very readily soluble in ether, benzene, or chloroform,

fairly readily so in alcohol, light petroleum, or acetic acid, and insoluble in water. It is rapidly hydrolysed when heated with aqueous sodium hydroxide, yielding oxalic acid and *β-thymomenthol*, a crystalline solid melting at 29°:

0·2183 gave 0·5769 CO_2 and 0·2014 H_2O. C = 72·1; H = 10·3.
$C_{22}H_{38}O_4$ requires C = 72·1; H = 10·4 per cent.

From the Δ^8-menthene a menthadiene was prepared in the following manner: A solution of the hydrocarbon (1 mol.) in about four times its weight of glacial acetic acid was cooled with ice-water, and a cooled solution of bromine (1 mol.) in the same solvent slowly added. The product was poured into water, and the *menthene dibromide*, $C_{10}H_{18}Br_2$, which separated as a heavy, oily liquid, extracted with ether. The ethereal solution was washed and dried, the ether removed, and the residual liquid distilled under diminished pressure. The dibromide is a colourless, rather viscous liquid, which boils at 125-—128°/30 mm. It is unstable, quickly becoming dark in colour.

The dibromide was heated for several hours on the water-bath under a reflux condenser with excess of alcoholic potassium hydroxide. When no further separation of potassium bromide was observed, the contents of the flask were distilled in a current of steam, and the oily liquid which passed over was separated from the condensed water by agitation with light petroleum. The solution was dried, the petroleum removed by distillation, and the residual liquid purified by repeated distillation over sodium.

The *menthadiene*, $C_{10}H_{16}$, obtained in this manner is a colourless liquid with a pleasant odour somewhat like that of limonene, and has the following constants: boiling point 173·5° under atmospheric pressure, D_{20}^{20} 0·8337, n_D 1·46539. It at once reduces potassium permanganate in the cold, and unites additively with bromine, but it does not form a stable tetrabromide at the ordinary temperature, for when more than two atomic proportions of bromine are added, evolution of hydrogen bromide begins. It does not appear to form a nitrosite under the usual conditions. On exposure to the air it absorbs oxygen fairly rapidly:

0·2555 gave 0·8206 CO_2 and 0·2797 H_2O. C = 87·7; H = 12·1.
0·1876 „ 0·6064 CO_2 „ 0·2070 H_2O. C = 88·1; H = 12·2.
$C_{10}H_{16}$ requires C = 88·2; H = 11·8 per cent.

Since Δ^8-menthene dibromide has the formula

$$\begin{array}{l} CH_2\cdot CHMe\text{—}CH_2 \\ | \qquad\qquad\qquad\; | \\ CH_2\cdot CBrPr^{\beta}\cdot CHBr \end{array}$$

probably the menthadiene prepared from it by elimination of two

molecules of hydrogen bromide in the manner described above is the $\Delta^{2:4}$-isomeride, with the formula: $\begin{array}{l} CH_2\cdot CHMe\cdot CH \\ | \qquad\qquad\quad \| \\ CH{=}CPr^{\beta}\cdot CH \end{array}$.

From menthol, through menthyl chloride, Birkenheim (*Ber.*, 1892, **25**, 690) prepared a hydrocarbon, $C_{10}H_{18}$, with the following constants: boiling point 170°, D_{20}^{20} 0·8160, n_D 1·4536. By addition of bromine to this compound and subsequent elimination of hydrogen bromide, he obtained a hydrocarbon, $C_{10}H_{16}$, which boiled at 172—174° and had D_{20}^{20} 0·8408. There can be little doubt that the menthene and menthadiene which we prepared synthetically from thymol are identical with the corresponding hydrocarbons which Birkenheim obtained directly from menthol.

Preparation of 1:3-*Diethyl*cyclo*hexadiene from Phenol.*

Considering that it would be of interest to compare the properties of the terpenes with those of isomeric hydrocarbons of the formula $C_{10}H_{16}$, we proceeded, in the first instance, to prepare a diethyl*cyclo*hexadiene from phenol in the following manner:

A quantity of 3:5-diethylphenol was prepared by condensing phenol with diethyl ether in presence of aluminium chloride, according to Jannasch and Rathjen's method (*Ber.*, 1899, **32**, 2392), and a mixture of the vapour of this compound and hydrogen was passed through a tube containing finely divided nickel and heated to a temperature of 160—170°. A colourless liquid collected in the cooled receiver, which, after purification by fractional distillation, proved to be principally composed of 1:3-*diethyl*cyclo*hexan*-5-*ol*, $CH_2{<}{\begin{array}{l}CHEt\cdot CH_2\\CHEt\cdot CH_2\end{array}}{>}CH\cdot OH$. This compound is a mobile, colourless liquid, with an odour somewhat like that of peppermint. It boils at 203—205° under atmospheric pressure, and has D_{20}^{20} 0·8945 and n_D 1·46450:

0·1728 gave 0·4851 CO_2 and 0·1915 H_2O. C = 76·6; H = 12·3.

$C_{10}H_{20}O$ requires C = 76·9; H = 12·8 per cent.

The bulk of the diethyl*cyclo*hexanol was boiled for several days under a reflux condenser with anhydrous oxalic acid, and when the dehydration of the alcohol appeared to be complete, the contents of the flask were distilled in a current of steam. A colourless, oily liquid passed over, and was separated from the condensed water by means of ether, while a small quantity of a non-volatile substance was left in the flask. The ethereal solution was dried, the ether removed by distillation, and the remaining liquid fractionally distilled. The principal fraction was redistilled several times over sodium, and finally a liquid of almost constant boiling point was obtained, which gave the following results on analysis:

0·2534 gave 0·8130 CO_2 and 0·2794 H_2O. C=87·5; H=12·3.
0·2848 „ 0·9131 CO_2 „ 0·3140 H_2O. C=87·4; H=12·3.
$C_{10}H_{18}$ requires C=87; H=13 per cent.

It appears from these numbers that the liquid consisted for the most part of 1:3-*diethyl*cyclo*hexene*, $C_{10}H_{18}$, but contained also a little diethyl*cyclo*hexadiene, $C_{10}H_{16}$, from which, owing to the proximity of their boiling points, it could hardly be separated by fractional distillation. The latter was probably derived from a little diethyl*cyclo*hexenol present in the specimen of diethyl*cyclo*-hexanol which was used for the preparation. However, it is worth noting in this connexion that, by the action of phosphoric oxide on menthone, Birkenheim (*loc. cit.*) obtained a similar mixture of hydrocarbons which gave on analysis: C=87·7, 87·8; H=12·3, 12·4, and drew the conclusion that both the compounds $C_{10}H_{18}$ and $C_{10}H_{16}$ are formed from menthone under the conditions mentioned.

The specimen of diethyl*cyclo*hexene, prepared as described above and apparently not quite pure, was a colourless liquid with a peculiar odour faintly resembling that of the menthene obtained from thymol. It boils at 163—166° under atmospheric pressure, and has D^{20}_{20} 0·83141 and n_D 1·46519. Taking into account its mode of formation, it is obviously the Δ^4-isomeride,

$$CH_2<\begin{matrix}CHEt\cdot CH_2\\CHEt-CH\end{matrix}>CH.$$

The non-volatile residue from the steam distillation of the dehydration product probably consisted of diethyl*cyclo*hexyl oxalate. It was extracted by means of ether, and, after removal of the ether, the oily liquid which remained was subjected to distillation, with the result that it underwent decomposition and yielded more of the hydrocarbon.

The next step was to prepare *diethyl*cyclo*hexene dibromide*, $C_{10}H_{18}Br_2$, and to eliminate two molecules of hydrogen bromide from one molecule of this compound. A cooled solution of bromine (1 mol.) in glacial acetic acid was slowly added to an ice-cold solution of diethyl*cyclo*hexene (1 mol.) in the same solvent. After a short time the solution was poured into water, and the dibromide which separated was collected and washed with water. It is a heavy, colourless, oily liquid, which begins to decompose on keeping. The dibromide was heated on the water-bath under a reflux condenser with excess of alcoholic potassium hydroxide, and when the reaction appeared to be completed steam was passed through the mixture. The oily liquid which passed over was extracted from the condensed water by means of light petroleum, the extract dried, the light petroleum removed by distillation, and the residual liquid fractionally distilled. The principal fraction was purified by

repeated distillation over sodium, and finally a liquid of constant boiling point was obtained, which analysis proved to be the desired hydrocarbon:

$$0{\cdot}1143 \text{ gave } 0{\cdot}3699\ CO_2 \text{ and } 0{\cdot}1196\ H_2O. \quad C=88{\cdot}3;\ H=11{\cdot}6.$$
$$C_{10}H_{16} \text{ requires } C=88{\cdot}2;\ H=11{\cdot}8 \text{ per cent.}$$

The 1:3-*diethyl*cyclo*hexadiene*, $C_{10}H_{16}$, thus obtained is a colourless liquid with a pleasant odour, and has the following constants: boiling point 166—168° under atmospheric pressure, D_{20}^{20} 0·8659 n_D 1·47575. The figure for the specific gravity is perhaps incorrect, as the quantity of material was too small for an accurate determination. The hydrocarbon is unsaturated, reducing at once an alkaline solution of potassium permanganate, and uniting additively with bromine. It also appears to resinify on exposure to the air. Since it is formed by elimination of hydrogen bromide from the dibromide of 1:3-diethyl-Δ^4-*cyclo*hexene (I), it most probably is 1:3-diethyl-$\Delta^{3:5}$-*cyclo*hexadiene (II):

$$CH_2{<}\begin{matrix}CHEt{-}CH_2\\ CHEt{\cdot}CHBr\end{matrix}{>}CHBr \longrightarrow CH_2{<}\begin{matrix}CHEt{\cdot}CH\\ CEt{=}CH\end{matrix}{>}CH$$

(I.) (II.)

It is our intention to examine more fully the character of this hydrocarbon and of some of its isomerides.

We take this opportunity of expressing our thanks to the Carnegie Trustees for a grant which defrayed most of the expense of this work.

CHEMISTRY DEPARTMENT,
THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

CCXLIV.—*The Velocity of Addition of Alkyl Bromides to Cyclic Tertiary Bases.*

By FRANK STEVENSON LONG.

DURING the last twenty years many investigations have been carried out on the reactivity of various alkyl halides. Summaries of these will be found in Burke and Donnan's paper (Trans., 1904, **85**, 555), showing that the reactivity of the halide exhibits in general no simple relation to its chemical constitution. Much of the more recent research was foreshadowed by the work of Lengfeld (*Amer. Chem. J.*, 1889, **11**, 40), in which the orders of stability towards alkalis on the one hand, and towards silver nitrate and nitric acid

on the other, were contrasted. The relative stabilities in ascending order of magnitude were given as:

(1) Towards alkalis: ethyl, propyl, butyl, *iso*amyl, *iso*butyl, and *iso*propyl.

(2) Towards silver nitrate and acids: *iso*propyl, ethyl, propyl, butyl, *iso*amyl, and *iso*butyl.

These relationships have, in the main, been confirmed by more recent work. As the second order seemed to be the more general, Lengfeld inclined to the belief that the protective influence of the $\cdot CHMe_2$ group apparent in the reactions of *iso*amyl, *iso*butyl, and *iso*propyl compounds towards alkalis was merely a coincidence.

In view of the discovery by Burke and Donnan (*Zeitsch. physikal. Chem.*, 1909, **69**, 148) that the reaction between silver nitrate and alkyl halides is not a simple bimolecular one, it seemed possible that the former series of stabilities (that is, towards alkalis) might be the more normal one, and that the eccentricity of the *iso*propyl compound might be due to some action other than simple replacement of the halogen.

Seeing that the number of velocity constants of addition of cyclic tertiary bases to alkyl halides determined by Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 411) was small compared with the number determined, using open-chain secondary and tertiary bases, it was thought most useful to utilise this method of investigating the problem. As it was found that quinoline and pyridine combine at an easily measurable rate below 100° with alkyl bromides in *iso*amyl-alcoholic solution, it was decided to adhere to these conditions throughout.

A few preliminary investigations showed that the reaction was strictly bimolecular, and that the velocity constant was unaltered by the addition of excess of either of the reacting substances.

The velocity constants for these three bromides at 92·5—92·7° are given in the following table:

	*iso*Amyl bromide.	*iso*Butyl bromide	*iso*Propyl bromide.
Pyridine	0·175	0·0246	0·0708
β-Picoline	0·138	0·0178	0 0571
α-Picoline	0·071	0·0127	0·0339
Quinoline	0·022	0·0048	0·0138

Thus, *iso*amyl bromide reacts, on the average, seven times and *iso*propyl bromide three times more rapidly than *iso*butyl bromide.

Before considering this result it will be best to take into account the relative reactivities determined by other workers. In the following table these are expressed approximately, taking the smallest velocity constant in each case as unity.

Observer :	*n*-Propyl.	*iso*Propyl.	*iso*Butyl.	*iso*Amyl.	Reaction with :
Wislicenus (*Annalen*, 1882, **212**, 239)	—	2	1	—	Sodioacetoacetic ester
Lengfeld (*Amer. Chem. J.*, 1889, **11**, 40)	4	1	between 1 and 2	2	*N*/10-sodium hydroxide
Brussoff (*Zeitsch. physikal. Chem.*, 1900, **34**, 129)	—	1	1	—	2*N*-alcoholic potassium hydroxide
Slator and Twiss (Trans., 1909, **95**, 93)	16	1	—	—	Sodium thiosulphate
Lengfeld (*loc. cit.*)	3·5	9	1	3	Silver nitrate and nitric acid
Burke and Donnan (Trans., *loc. cit.*)	8	enormously large	1	4	Alcoholic silver nitrate
Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1892, **22**, 346)	10	1	2	—	Triethylamine
Wedekind (*Annalen*, 1901, **90**, 116)	3·6 *	1·8 *	1 *	—	Dimethylaniline
Present communication	14	3	1	7	—

* These represent relative percentage yields. In some cases the iodides were used.

All the anomalies in the above table will be seen to be due to the *iso*propyl compound. This is perhaps not so very remarkable, seeing that it differs from the others by being a secondary compound; its reactivity towards pyridine is indeed slightly less than that of the bromide of methylhexylcarbinol, the only other secondary bromide examined.

For the other alkyl compounds we have the reactivity increasing normally as the halogen atom is removed from the influence of the two methyl groups.

The bases examined exhibit steric influences in a remarkably regular manner. With every halogen compound employed the reactivities of the various bases are in the same relative order, the relationships being in many cases almost quantitative. This order, commencing with the most reactive, is: Pyridine, β-picoline, α-picoline, lutidine, quinoline, and 2-methylquinoline.

Experimental.

The *iso*amyl alcohol used as solvent was Kahlbaum's "Pyridine-free" quality. The final adjustment of volume was made after the graduated flasks had been immersed in the thermostat for some time. Times were therefore reckoned from that of the first titration. At definite intervals of time one-tenth of the volume was withdrawn by a warmed pipette, and the reaction arrested by adding cold distilled water. Volhard's thiocyanate method was found to be the most convenient.

The values of the velocity constant were determined from the formula for a bimolecular reaction, namely:

$$\frac{1}{(\theta_2-\theta_1)}\left(\frac{1}{T_\infty - T_{\theta_2}} - \frac{1}{T_\infty - T_{\theta_1}}\right) \times F = k,$$

where θ_1, θ_2 are the times in hours, and T_∞ is the calculated titration value when the action was complete.

The titration numbers are converted into normality figures by multiplying by the appropriate factor F.

The Effect of Excess of each Reacting Substance.

92° in thermostat. *iso*Amyl bromide (b. p. 117·5—118·5°) and pyridine (b. p. 114·1—114·5°).

I. 3·02 Grams of *iso*amyl bromide. 1·58 Grams of pyridine. Made up to 100 c.c. with *iso*amyl alcohol.

θ	0	0·33	1·25	3·25	6·50	8·00
$20-T$.........	—	19·91	19·25	17·90	16·05	15·70
k	—	—	0·176	0·181	0·189	0·170

Mean $k=0·179$

II. 6·04 Grams of *iso*amyl bromide. 1·58 Grams of pyridine in 100 c.c.

θ	0	0·25	3·25	6·50	8·00
$20-T$	—	19·89	16·50	13·90	12·20
k	—	—	0·170	0·140	0·170

Mean $k=0·170$ (omitting 2nd).

III. 3·02 Grams of *iso*amyl bromide. 3·16 Grams of pyridine in 100 c.c.

θ	0	3·25	6·50	8·0
$20-T$	19·89	16·00	13·60	11·85
k................ ..	—	0·180	0·162	0·180

Mean $k=0·174$.

These results were sufficient to show that the presence of excess of either of the constituents has no abnormal influence on the velocity of the reaction. The constants for II and III were obtained from the formula:

$$\frac{1}{\theta_2-\theta_1}\left(\log\frac{a-x_2}{b-x_2} - \log\frac{a-x_1}{b-x_1}\right) = (a-b)k.$$

Determination of the Order of the Reaction.

IV. 3·02 Grams of *iso*amyl bromide. 1·58 Grams of pyridine in 100 c.c. Temperature 94—95° in water-bath.

θ	0	1·5	2·5	2·83	18·6
$20 - T$	20·0	18·8	18·08	17·95	11·5
k	—	0·195	0·214	0·207	0·200

Mean $k = 0·204$.

V. 3·02 Grams of *iso*amyl bromide. 1·58 Grams of pyridine in 50 c.c. 5 C.c. each titration.

θ	0	1·5	2·5	3·5	5	18·5	22
$20 - T$...	20·0	17·94	16·85	15·91	14·70	7·96	7·15
k	—	0·191	0·187	0·184	0·180	0·205	0·204

Mean $k = 0·192$.

(*a*) *Calculation of the Order by van't Hoff's Method.*—Using the change during the first 1·5 hours in each case for dC/dt we have:

$$\text{Order of reaction, } n = \frac{\log \frac{dC_1}{dt} - \log \frac{dC_2}{dt}}{\log \frac{C_1}{C_2}} = 1·8 \text{ nearly.}$$

This method is seriously affected by the errors of experiment.

(*b*) *Using the Formula of Noyes* (*Zeitsch. physikal. Chem.*, 1896, **19**, 599):

$$n = 1 + \frac{\log \theta_1 - \log \theta_2}{\log C_{20} - \log C_{10}},$$

where θ_1 and θ_2 are the times for the same fractional part of the reaction to be completed when the initial concentrations are C_{10} and C_{20} respectively. A mean value of $n = 1·90$ was obtained graphically.

The reaction may therefore be regarded as strictly bimolecular.

The velocity determinations given below were carried out, except where otherwise stated, at 92·6° in a thermostat; the concentrations were varied from $N/5$ to $4N/5$ in order to keep the velocity between measurable limits. As above, θ represents the time interval in hours, T the titration value in c.c. of $N/10$-silver nitrate, and k the velocity constant. In experiments VII and VIII the value of the velocity constant at 92·6° was obtained by multiplying the value at 91·5° by the known ratio of the values for pyridine and *iso*amyl bromide at these temperatures.

VI. iso*Amyl Bromide and Pyridine* ($2N/5$).

θ	0	1	2	3	4·06	5	7·25
$1/20 - T$	0·05311	0·05650	0·06053	0·06378	0·06812	0·07168	0·08130
k	—	0·170	0·185	0·182	0·186	0·186	0·170

Mean value of $k = 0·180$.

VII. iso*Amyl Bromide and α-Picoline* ($N/5$) *at* 91·5°.

θ	0	2·00	3	6·25	7·33	7·75	23·41
$20-T$ ...	19·70	19·20	18·95	18·19	18·03	17·80	15·07
k............	—	0·066	0·0676	0·0674	0·0641	0·0699	0·0690

Mean value of $k=0·0673$. Hence at 92·6° $=0·071$.

VIII. iso*Amyl Bromide and β-Picoline* ($N/5$) *at* 91·5°

θ	0	2	3·25	6·25	7·3	8·25
$20-T$ ...	19·82	18·85	18·27	16·99	16·77	16·50
k	—	0·132	0·1309	0·1353	0·1265	0·1244

Mean value of $k=0·1298$ ∴ Value at 92·6° $=0·138$.

IX. iso*Amyl Bromide and Quinoline* ($4N/5$) *at* 92·6°.

θ...	0	2	16	17	25	39	49·6
$1/20-T$ ...	0·05200	1·05376	0·06549	0·06645	0·07675	0·09242	0·10427
k	—	0·0220	0·0203	0·0205	0·0238	0·0250	0·0214

Mean value of $k=0·0222$.

X. iso*Butyl Bromide and β-Picoline* ($2N/5$).

θ........................	0·66	15·7	17 2	23·7
$1/10-T$...............	0·1044	0·1151	0·1164	0·1203
k...................... ..	—	0·0178	0·0182	0·0173

Mean value of $k=0·0178$.

XI. iso*Butyl Bromide and Pyridine* ($2N/5$).

θ	0	0·5	4·25	5·5	7	22·5	43·5
$1/8-T$ ...	0·1318	0·1321	0·1366	0·1389	0·1406	0·1563	0·1805
k	—	—	0·023	0·0258	0·0250	0·0220	0·0224

Mean value of $k=0·0246$.

XII. iso*Butyl Bromide and α-Picoline* ($2N/5$).

θ.........................	0	12	23·16	24·0
$1/10-T$	0·1031	0·1093	0·1149	0·1149
k........................	—	0·0130	0·0127	0·0125

Mean value of $k=0·0127$.

XIII. iso*Butyl Bromide and Quinoline* ($4N/5$).

θ	0	2·5	3·0	4	18·1	28·1
$1/20-T$	0·05277	0·05325	0·05333	0·05350	0·05621	0·05817
k	—	0·0048	0·0047	0·0046	0·0048	0·0049

Mean value of $k=0·0048$.

XIV. iso*Propyl Bromide and Pyridine* ($2N/5$).

θ	0	0·56	1	3	4	5	6
$1/10-T$...	0·10137	0·10289	0·10411	0·11012	0·11270	0·11559	0·11872
k	—	0·0690	0·0685	0·0727	0·0708	0·0711	0·0725

Mean value of $k=0·0708$.

XV. *iso*Propyl Bromide and α-Picoline (2N/5).

θ	0	1·05	3	4	5	6	25
$1/10 - T$...	0·10152	0·10280	0·10554	0·10707	0·10883	0·11050	0·13263
k	—	0·0305	0·0335	0·0347	0·0365	0·0372	0·0311

Mean value of $k = 0·0339$.

XVI. *iso*Propyl Bromide and β-Picoline (2N/5).

θ.................	0	1·5	2	3·33	4·33	5
$1/10 - T$	0·10063	0·10421	0·10494	0·10819	0·11080	0·11203
k	—	0·0596	0·0540	0·0567	0·0585	0·0570

Mean value of $k = 0·0571$.

XVII. *iso*Propyl Bromide and Quinoline (4N/5).

θ	0	1	2	3	4	22	25
$1/20 - T$...	0·05016	0·05071	0·05118	0·05171	0·05227	0·06313	0·06574
k...........	—	0·0137	0·0128	0·0129	0·0132	0·0147	0·0155

Mean value of $k = 0·0138$.

In these experiments with *iso*propyl bromide (b. p. 59·5—60°) there are indications of a tendency for the "velocity constant" to increase with time. With the far more reactive propyl bromide (b. p. 70—71°) this tendency was very pronounced, especially when the base was also rather volatile; for example, with the slightly volatile quinoline we have:

XVIII. n-*Propyl Bromide and Quinoline* (2N/5).

θ	0	19·43	20·63	21·9	71·4
$1/10 - T$............	0·1011	0·1543	0·1580	0·1631	0·3952
k.....................	—	0·0685	0·0690	0·0708	0·103

whilst with pyridine:

XIX. *Propyl Bromide and Pyridine* (2N/5).

θ	1·02	3	4·03	7·02	7·50	8·5
$1/10 - T$ ...	0·1155	0·1495	0·1712	0·2421	0·2625	0·2907
k	0·388	0·412	0·445	0·501	0·562	0·66

The effect would appear to be due to a concentrated film of the reacting substances in the unfilled portion of the flask. This film would become larger as the volume of solution remaining became less, so that the reaction would seem to increase in velocity as found. If this explanation be correct, it would indicate that no serious error due to this cause resulted in the other experiments where k remained practically constant.

2-Methylquinoline (b. p. 244—245°) reacted so slowly that only

the commencement of its reactions could be followed. Figures were thus obtained which are, however, for this reason untrustworthy; thus with *iso*amyl bromide:

XX. iso*Amyl Bromide and 2-Methylquinoline* ($4N/5$).

θ	0·5	14·75	25·5	26
$1/20-T$	0·05053	0·05319	0·05562	0·05571
k	—	0·0047	0·0050	0·0051

The mean value for k (0·0049) gives an indication of the relative velocity. The following determinations are given for comparative purposes:

XXI. sec-*Octyl Bromide and Pyridine* ($2N/5$).

θ	0	2·33	4	5	18·4
$1/10-T$	0·1018	0·1096	0·1159	0·1191	0·1712
k	—	0·084	0·088	0·0865	0·94

Mean value for $k=0·088$.

XXII. iso*Amyl Iodide* ($N/5$) *and Pyridine* ($2N/5$).

θ	0	0·5	1·5	2·6	7·2
T	0·10	0·43	0·87	1·39	2·86
k	—	0·357	0·301	0·310	0·348

Where $k=2·303\times\frac{5}{\theta_2-\theta_1}\left(\log_{10}\frac{10-T_2}{5-T_2}-\log_{10}\frac{10-T_1}{5-T_1}\right)$.

Mean value of $k=0·329$.

XXIII. iso*Amyl Chloride and Pyridine* ($4N/5$).

θ	0	18·7	19	22·5	28
$1/20-T$	0·05005	0·05583	0·05627	0·05698	0·05879
k	—	0·0077	0·0081	0·0077	0·0079

Mean value of $k=0·00785$.

I desire, in conclusion, to express my indebtedness to Professor J. T. Hewitt for kind interest and valuable advice. My thanks are also due to the Research Fund Committee of the East London College for a grant which defrayed the cost of the materials employed.

East London College.

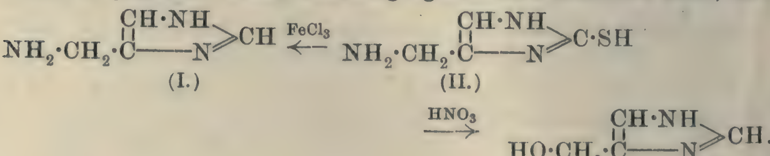
CCXLV.—*Aminoalkylglyoxalines.*

By Frank Lee Pyman.

In view of the great physiological activity of 4(or 5)-β-aminoethylglyoxaline (compare Dale and Laidlaw, *J. Physiol.*, 1910, **41**, 318), the preparation of several of its homologues has been carried out, and these have been physiologically tested by Dr. P. P. Laidlaw, of the Wellcome Physiological Research Laboratories, to whom the author is indebted for the results given in this paper. In this connexion the recent preparation of other homologues of this base by Ewins (this vol., p. 2052) may be noted.

Barger and Dale (*J. Physiol.*, 1910, **41**, 19), in dealing with the relationship between the chemical constitution of the amines and their physiological action, have shown that the activity varies greatly with the length of the side-chain; in the fatty series the maximum of activity is attained at hexylamine, whilst the most active phenylalkylamine is phenylethylamine, having a fatty side-chain of two carbon atoms. It appeared, therefore, of interest to determine the optimum length of side-chain for physiological effect in the aminoalkylglyoxalines. For comparison with 4(or 5)-β-aminoethylglyoxaline, 4(or 5)-aminomethylglyoxaline and 4(or 5)-γ-aminopropylglyoxaline were required, but since the latter was not readily accessible its methyl homologue, 4(or 5)-γ-aminobutylglyoxaline, was prepared and tested in its place. Compared with 4(or 5)-β-aminoethylglyoxaline, the activity of these bases proved to be negligible.

4(or 5)-Aminomethylglyoxaline (I) has recently been described by Windaus and Opitz (*Ber.*, 1911, **44**, 1721), who prepared it by Curtius' method from glyoxaline-4(or 5)-acetic acid obtained from histidine. It may, however, readily be prepared synthetically by suitably oxidising 2-thiol-4(or 5)-aminomethylglyoxaline (II). It has previously been shown (this vol., p. 669) that the customary method of oxidising thiolglyoxalines to glyoxalines by means of nitric acid leads, in the case of this compound, to 4(or 5)-hydroxymethylglyoxaline (III). If, however, an oxidising agent not producing nitrous acid were employed, the formation of 4(or 5)-aminomethylglyoxaline would be possible. Other oxidising agents were therefore tried, and



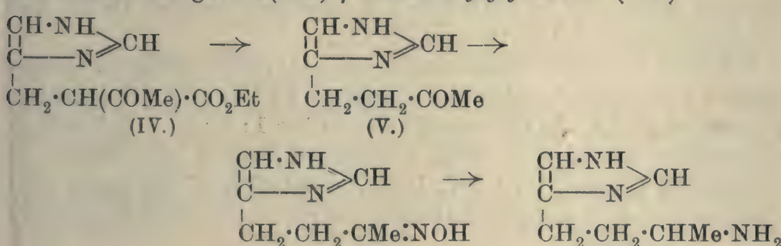
(I.) (II.) (III.)

it was found that ferric chloride in calculated quantity oxidised 2-thiol-4(or 5)-aminomethylglyoxaline to 4(or 5)-aminomethylglyoxaline in a yield amounting to more than 50 per cent. of the theoretical:

Potassium permanganate is unsuitable for the oxidation of 2-thiol-4(or 5)-aminomethylglyoxaline to 4(or 5)-aminomethylglyoxaline, for it readily attacks the former substance, causing complete rupture of the glyoxaline ring; cold dilute aqueous solutions of potassium permanganate are immediately decolorised by 2-thiol-4(or 5)-aminomethylglyoxaline, but not by 4(or 5)-aminomethylglyoxaline or other glyoxalines not containing the 2-thiol group. This difference in behaviour is ascribed to the possibility of the thiol base reacting in the tautomeric thiocarbamide form as an unsaturated compound.

4(or 5)-γ-*Aminobutylglyoxaline* was readily prepared as follows:

Ethyl 4(or 5)-glyoxalinemethylacetoacetate (IV) (this vol., p. 1392) was converted into the corresponding ketone, 4(or 5)-γ-*ketobutylglyoxaline* (V), by hydrolysis with hydrochloric acid. This was next transformed into the oxime, 4(or 5)-γ-*oximinobutylglyoxaline* (VI), which on reduction by means of sodium amalgam and acetic acid gave 4(or 5)-γ-*aminobutylglyoxaline* (VII):



(IV.) (V.) (VI.) (VII.)

A quantity of αβ-bis[4(or 5)-glyoxaline]-propionitrile (VIII) (this vol., p. 677) which is formed as a by-product in the preparation of 4(or 5)-cyanomethylglyoxaline being available, it was thought of interest to reduce it to βγ-*bis*[4(or 5)-*glyoxaline*]-*propylamine* (IX), which may be regarded as an aminoethylglyoxaline containing a glyoxalinemethyl substituent. This reduction was carried out with sodium and alcohol, and the desired base was obtained, together with another compound, which was probably *αβ-bis*[4(or 5)-*glyoxaline*]-*propionic acid* (X):

$C_3H_3N_2{\cdot}CH_2{\cdot}CH(CN){\cdot}C_3H_3N_2 \longrightarrow$
(VIII.)

$C_3H_3N_2{\cdot}CH_2{\cdot}CH(CH_2{\cdot}NH_2){\cdot}C_3H_3N_2$, and
(IX.)

$C_3H_3N_2{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}C_3H_3N_2$.
(X.)

The physiological action of $\beta\gamma$-bis[4(or 5)-glyoxaline]-propylamine is very slight compared with that of 4(or 5)-β-aminoethylglyoxaline.

The two isomeric *N*-methyl derivatives of 4(or 5)-β-aminoethylglyoxaline in which the methyl group substitutes the imino-hydrogen atom of the glyoxaline ring were next prepared. These compounds, 1-methyl-4(and 5)-aminoethylglyoxaline (XI and XII),

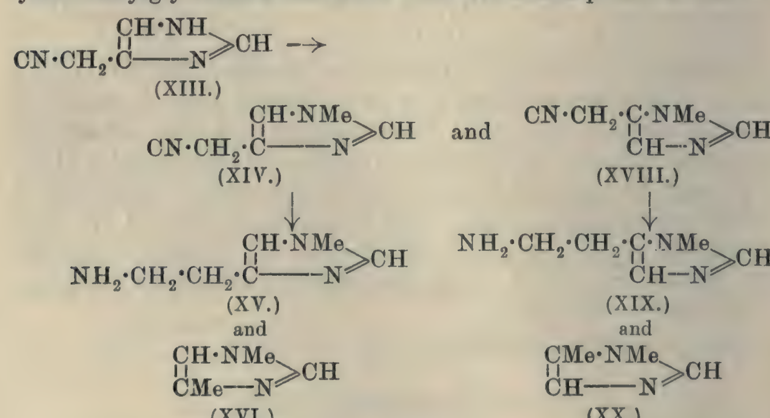
(XI.) (XII.)

were obtained by reduction of the corresponding methylcyanomethylglyoxalines. Their physiological action is negligible compared with that of 4(or 5)-β-aminoethylglyoxaline.

4(or 5)-Cyanomethylglyoxaline (XIII) (this vol., p. 676) yields on methylation with methyl sulphate and alkali a mixture of the 1:4- and 1:5-methylcyanomethylglyoxalines, from which the former can readily be obtained in a pure state, and the latter less readily by fractional crystallisation of the picrates.

1-*Methyl*-4-*cyanomethylglyoxaline* (XIV) gave on reduction with sodium and alcohol 1-*methyl*-4-β-*aminoethylglyoxaline* (XV), together with small quantities of 1:4-dimethylglyoxaline (XVI) and 1-*methylglyoxaline*-4-*acetic acid* (XVII).

1-*Methyl*-5-*cyanomethylglyoxaline* (XVIII) when similarly treated yielded 1-*methyl*-5-β-*aminoethylglyoxaline* (XIX) and 1:5-dimethylglyoxaline (XX). As the constitution of the 1:4- and 1:5-dimethylglyoxalines has already been determined with a high degree of probability (Trans., 1910, **97**, 1814), orientation of the methylated cyanomethylglyoxalines and their other reduction products follows:



1-Methylglyoxaline-4-acetic acid may readily be prepared by hydrolysing 1-methyl-4-cyanomethylglyoxaline with alkali. Its

ester, *ethyl* 1-*methylglyoxaline*-4-*acetate*, was prepared by the action of alcoholic hydrogen chloride on 1-methyl-4-cyanomethylglyoxaline:

$$\begin{array}{l}\quad\quad\quad\quad\;\; CH\cdot NMe \\ \quad\quad\quad\quad\;\; \| \quad\quad\quad\quad > CH \\ CO_2H\cdot CH_2\cdot C \text{———} N \end{array} \qquad\qquad \begin{array}{l} CO_2H\cdot CH_2\cdot C\cdot NMe \\ \quad\quad\quad\quad\quad\;\; \| \quad\quad\quad > CH \\ \quad\quad\quad\quad\quad\;\; CH\text{—}N \end{array}$$

(XVII.) (XXI.)

1-*Methylglyoxaline*-5-*acetic acid* (XXI) was obtained by hydrolysing 1-methyl-5-cyanomethylglyoxaline with alkali.

Experimental.

Oxidation of 2-*Thiol*-4(or 5)-*aminomethylglyoxaline to* 4(or 5)-*Aminomethylglyoxaline.*

1·29 Grams of 2-thiol-4(or 5)-aminomethylglyoxaline (this vol., p. 672) were dissolved in 50 c.c. of water, added to a solution of 9·8 grams of ferric chloride in 100 c.c. of water, and the mixture digested for half an hour in the water-bath. Thirty c.c. of 10 per cent. aqueous sodium carbonate were then added, followed by a hot solution of 4·6 grams of picric acid in 100 c.c. of boiling water. The liquor was then boiled with a little animal charcoal and filtered, and on cooling 3·2 grams of pure 4(or 5)-aminomethylglyoxaline dipicrate separated in the first crop; this quantity represents 56 per cent. of the theoretical yield.

4(or 5)-Aminomethylglyoxaline dipicrate crystallises from water in hexagonal or diamond-shaped plates, which melt at 210—211° (corr.). It contains $1H_2O$, which is lost at 120°, but not at 100°. The water of crystallisation in this salt is not mentioned by Windaus and Opitz (*Ber.*, 1911, **44**, 1723), who give the melting point as 209°:

0·1749 * lost *nil* at 100°, lost 0·0054 at 120°. $H_2O = 3·1$.

0·2064 † gave 0·2550 CO_2 and 0·0496 H_2O. $C = 33·7$; $H = 2·7$.

$C_4H_7N_3,2C_6H_3O_7N_3,H_2O$ requires $C = 33·5$; $H = 2·6$; $H_2O = 3·1$ per cent.

4(or 5)-Aminomethylglyoxaline dihydrochloride was prepared by treating the picrate with hydrochloric acid, removing the picric acid by means of ether, evaporating the acid liquor to dryness, and crystallising the residue from water. It separates from water in colourless, prismatic needles, which contain $\frac{1}{2}H_2O$, and after drying at 100° melt at 244—245° (corr.) after sintering from about 235°. Its aqueous solution is strongly acid:

0·1262, air-dried salt, lost 0·0068 at 100°. $H_2O = 5·4$.

$C_4H_7N_3,2HCl,\frac{1}{2}H_2O$ requires $H_2O = 5·0$ per cent.

* Air-dried. † Dried at 100°.

For anhydrous salt: Found, C=28·0; H=5·6. Calc., C=28·2; H=5·3 per cent.

Windaus and Opitz (*loc. cit.*), who crystallised this salt from a mixture of methyl alcohol and ether, do not mention any water of crystallisation; they state that on heating, the salt sinters from 236° onwards.

4(or 5)-*Aminomethylglyoxaline hydrogen oxalate* crystallises from water in monoclinic, hexagonal plates, which decompose at 218° (corr.). It is anhydrous, and is sparingly soluble in cold water:

0·2478 gave 0·3158 CO_2 and 0·0898 H_2O. C=34·8; H=4·1.

$C_4H_7N_3,2C_2H_2O_4$ requires C=34·7; H=4·0 per cent.

4(or 5)-γ-*Ketobutylglyoxaline* [4(or 5)-*Glyoxaline-ethyl Methyl Ketone*], $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot \overset{\displaystyle CH\cdot NH}{\overset{\|}{C}\!-\!\!-\!\!-N}\!\!>\!CH.$

Fifteen grams of ethyl 4(or 5)-glyoxalinemethylacetoacetate hydrogen oxalate (this vol., p. 1392) were converted into the base, and this boiled under a reflux condenser for three hours with 60 c.c. of hydrochloric acid and 90 c.c. of water. The liquid was then evaporated to dryness under diminished pressure, and the residue dissolved in a little water, mixed with sodium carbonate, and extracted with chloroform. The extract after drying and distillation of the solvent left the ketone as a viscid, brown oil, which solidified on keeping, forming large, buff crystals, melting at 76—78°, and amounting to 4·4 grams; this yield is 64 per cent. of the theoretical.

4(or 5)-γ-*Ketobutylglyoxaline* crystallises from anhydrous ethyl acetate in stout, colourless, prismatic needles, which melt at 80—81° (corr.). It is very readily soluble in water, alcohol, acetone, or chloroform, readily so in ethyl acetate, and very sparingly so in ether or benzene:

0·1278 gave 0·2854 CO_2 and 0·0882 H_2O. C=60·9; H=7·7.

$C_7H_{10}ON_2$ requires C=60·8; H=7·3 per cent.

The *picrate* crystallises from water or alcohol in fine, yellow needles, which melt at 192—193° (corr.). It is very sparingly soluble in cold water or alcohol, but fairly readily so in hot water:

0·1088 gave 0·1702 CO_2 and 0·0370 H_2O. C=42·6; H=3·8.

$C_7H_{10}ON_2,C_6H_3O_7N_3$ requires C=42·5; H=3·6 per cent.

4(or 5)-γ-*Oximinobutylglyoxaline*,

$$HO\cdot N:CMe\cdot CH_2\cdot CH_2\cdot \overset{\displaystyle CH\cdot NH}{\overset{\|}{C}\!-\!\!-\!\!-N}\!\!>\!CH.$$

This oxime is readily prepared in good yield by heating on the water-bath an aqueous solution of the ketone with the calculated

amounts of hydroxylamine hydrochloride and sodium carbonate; on concentrating and cooling the solution, the oxime crystallises out, and is purified by recrystallisation from water.

4(or 5)-γ-*Oximinobutylglyoxaline* crystallises from water in clear, colourless plates, which melt at 152—153° (corr.). It is sparingly soluble in cold water or acetone, fairly readily so in alcohol or hot water, but very sparingly so in chloroform:

0·2134 gave 0·4284 CO_2 and 0·1407 H_2O. C=54·7; H=7·4.

$C_7H_{11}ON_3$ requires C=54·9; H=7·3 per cent.

The *picrate* crystallises from water in hard, spherical grains, which melt at 166—168° (corr.). This salt is sparingly soluble in cold, but readily so in hot, water.

4(or 5)-γ-*Aminobutylglyoxaline*,

$$\begin{array}{l} \qquad\qquad\qquad\qquad\quad\ \ CH{\cdot}NH \\ CH_3{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CH_2{\cdot}\overset{\|}{C}\text{———}N \end{array}\!\!>\!CH.$$

2·3 Grams of 4(or 5)-γ-oximinobutylglyoxaline were dissolved in 15 c.c. of alcohol and 5 c.c. of glacial acetic acid. Fifty grams of 3 per cent. sodium amalgam were then added, and the mixture well shaken and cooled with water. Enough water was supplied from time to time to dissolve the separated sodium acetate, and two further quantities, each of 5 c.c., of acetic acid and 50 grams of sodium amalgam were subsequently added. When the sodium amalgam had been used up, the liquor was diluted with about 100 c.c. of water, and poured into a hot solution of 7 grams of picric acid in 200 c.c. of water, when on cooling 4(or 5)-γ-aminobutylglyoxaline dipicrate crystallised out. After recrystallisation from water 4·1 grams of the pure salt were obtained, that is, 45 per cent. of the theoretical.

4(or 5)-γ-*Aminobutylglyoxaline dipicrate* crystallises from water in long, golden, somewhat serrated spikes, which melt at 247° (corr.) to a brown liquid, which then decomposes. This salt is anhydrous, and very sparingly soluble in cold, but fairly readily so in hot, water:

0·1163 gave 0·1638 CO_2 and 0·0350 H_2O. C=38·4; H=3·4.

$C_7H_{13}N_3,(C_6H_3O_7N_3)_2$ requires C=38·2; H=3·2 per cent.

Reduction of αβ-Bis[4(or 5)-*glyoxaline*]-*propionitrile.*

Nine grams of αβ-bis[4(or 5)-glyoxaline]-propionitrile hydrogen oxalate * were converted into the base in the manner previously described, and this was reduced by means of 5 grams of sodium

* This vol., p. 677; the formula of the base should read $C_9H_9N_5$.

and 75 c.c. of absolute alcohol. The reaction product was neutralised with hydrochloric acid, made strongly alkaline with sodium carbonate, evaporated to dryness under diminished pressure, and the residue completely extracted with absolute alcohol. After the removal of the bulk of the solvent, the extract was poured into a solution of 20 grams of picric acid in 500 c.c. of boiling water, when a viscous oil separated. After the solution had cooled somewhat it was decanted from the oil and filtered, when it deposited about 3 grams of crystals, melting at 195—200°. The very sparingly soluble oil also became crystalline on cooling, and was extracted with 500 c.c. of boiling water, filtered, and allowed to cool to about 50°, when 5·0 grams of orange needles, melting at 150—153°, separated; these were collected, and the mother liquor allowed to become quite cold, when a further 1·6 grams of crystals, melting at about 210°, separated.

The more sparingly soluble picrate was readily purified by crystallisation from water, and proved to be *βγ-bis*[4(or 5)-*glyoxaline*]-*propylamine tripicrate*; 3·4 grams of this salt were obtained in a pure state, decomposing at 158° (corr.), that is, 18 per cent. of the theoretical. The more easily soluble picrate was less readily purified; it melted and decomposed at 218—220° (corr.) when pure, and was probably *αβ-bis*[4(or 5)-*glyoxaline*]-*propionic acid dipicrate*:

0·1300, air-dried salt, lost 0·0072 at 100°. $H_2O = 5·5$.

$C_9H_{10}O_2N_4,(C_6H_3O_7N_3)_2,2H_2O$ requires $H_2O = 5·1$ per cent.

0·1010 * gave 0·1392 CO_2 and 0·0268 H_2O. C = 37·6; H = 3·0.

0·1232 * „ 0·1706 CO_2 „ 0·0331 H_2O. C = 37·8; H = 3·0.

$C_9H_{10}O_2N_4,(C_6H_3O_7N_3)_2$ requires C = 37·9; H = 2·4 per cent.

βγ-Bis[4(or 5)-*glyoxaline*]-*propylamine*, $C_3H_3N_2 \cdot CH_2 \cdot CH(CH_2 \cdot NH_2) \cdot C_3H_3N_2$.

The *tripicrate* crystallises from water in beautiful, orange-yellow, flat needles, which soften from 150° and decompose at 158° (corr.). This salt is sparingly soluble in hot, and very sparingly so in cold, water. It is anhydrous:

0·1330 gave 0·1786 CO_2 and 0·0330 H_2O. C = 36·6; H = 2·8.

$C_9H_{13}N_5,(C_6H_3O_7N_3)_3$ requires C = 36·9; H = 2·5 per cent.

The *trihydrochloride* was prepared by treating the picrate with hydrochloric acid and ether, and after evaporation of the excess of acid was obtained as a colourless varnish. This readily became crystalline when warmed with alcohol. The crystals were collected, dissolved in very little water, and hot alcohol added to the solution,

* Dried at 100°.

when the salt separated in beautiful, colourless, refracting prisms. The air-dried salt contains a molecule of water of crystallisation, which is not lost at 100°, but probably escapes at about 140°, for on heating the salt sinters at this temperature, but then remains unchanged until it melts at 235—237° (corr.). It is readily soluble in water, giving an acid solution, but is insoluble in absolute alcohol:

0·1382 gave 0·1730 CO_2 and 0·0730 H_2O. C=34·1; H=5·9.

0 1482 „ 0·1981 AgCl. Cl=33·1.

$C_9H_{13}N_5,3HCl,H_2O$ requires C=33·9; H=5·7; Cl=33·4 per cent.

Methylation of 4(or 5)-*Cyanomethylglyoxaline.*

Twenty grams of 4(or 5)-cyanomethylglyoxaline (this vol., p. 676) were dissolved in 80 c.c. of 10 per cent. aqueous sodium hydroxide, and shaken with 16 grams of methyl sulphate added gradually while the liquid was shaken and cooled by running water. Another 70 c.c. of 10 per cent. aqueous sodium hydroxide and 16 grams of methyl sulphate were then added. The clear brown liquor was completely extracted by chloroform, and the solvent removed from the extract, when a brown oil resulted. This was dissolved in water, and poured into 2100 c.c. of warm 2 per cent. picric acid solution, when most of the 1-*methyl*-4-*cyanomethylglyoxaline picrate* crystallised out at once in a pure state. On concentrating the mother liquors, 1-*methyl*-5-*cyanomethylglyoxaline picrate* separated out, mixed with small quantities of its isomeride, and it was purified by recrystallisation from water.

There were isolated 28·5 grams of 1-methyl-4-cyanomethylglyoxaline picrate, melting at 209—210° (corr.), and 9·9 grams of 1-methyl-5-cyanomethylglyoxaline picrate, melting at 156—157° (corr.), these quantities amounting to 43 and 15 per cent. of the theoretical respectively.

1-*Methyl*-4-*cyanomethylglyoxaline*, $\begin{array}{l} \quad\quad\quad\quad CH\cdot NMe \\ CN\cdot CH_2\cdot \overset{\|}{C}\text{———}N \end{array}\!\!>\!CH.$

This base crystallises from chloroform in clusters of plates, which melt at 34—36° (corr.). It is very deliquescent, and readily soluble in water and the usual organic solvents, with the exception of ether and light petroleum:

0·1337 * gave 0·2917 CO_2 and 0·0731 H_2O. C=59·5; H=6·1.

$C_6H_7N_3$ requires C=59·5; H=5·8 per cent.

The *hydrogen oxalate* crystallises from water or alcohol in

* Dried at 100°.

prismatic needles, which melt at 116—117° (corr.). It is readily soluble in water, but sparingly so in alcohol:

0·1503 gave 0·2496 CO_2 and 0·0572 H_2O. C=45·3; H=4·3.
0·1143 „ 19·6 c.c. N_2 at 18° and 759 mm. N=20·2.
$C_6H_7N_3,C_2H_2O_4$ requires C=45·5; H=4·3; N=19·9 per cent.

The *picrate* crystallises from water in flat, fern-like clusters of stout needles, or in rods of a rather pale yellow colour, which melt at 209—210° (corr.). It is anhydrous, and is very sparingly soluble in cold, but fairly readily so in hot, water:

0·1530 gave 0·2290 CO_2 and 0·0395 H_2O. C=40·8; H=3·0.
$C_6H_7N_3,C_6H_3O_7N_3$ requires C=41·1; H=2·9 per cent.

The *mercurichloride* and *mercuri-iodide* both readily crystallise from water in long needles.

1-*Methyl-5-cyanomethylglyoxaline*, $\begin{array}{l}CN\cdot CH_2\cdot C\cdot NMe \\ \quad\quad\quad\;\; CH{-}{-}N\end{array}\!\!>\!CH.$

This base was obtained as an oil, which did not crystallise when kept for several hours at 0°. It is readily soluble in water, alcohol, or chloroform.

The *hydrogen oxalate* crystallises from alcohol in prisms, which sinter slightly from 135°, and melt and effervesce at 139—140° (corr.). It is anhydrous. It is readily soluble in water, but sparingly so in alcohol:

0·1580 gave 0·2632 CO_2 and 0·0612 H_2O. C=45·4; H=4·3.
$C_6H_7N_3,C_2H_2O_4$ requires C=45·5; H=4·3 per cent.

The *picrate* crystallises from water in large, pale yellow, glistening leaflets, which melt at 156—157° (corr.). This salt is anhydrous, sparingly soluble in cold, but readily so in hot, water:

0·1507 gave 0·2284 CO_2 and 0·0411 H_2O. C=41·3; H=3·1.
$C_6H_7N_3,C_6H_3O_7N_3$ requires C=41·1; H=2·9 per cent.

1-*Methylglyoxaline-4-acetic Acid*, $\begin{array}{l}\quad\quad\quad\quad\quad\;\; CH\cdot NMe \\ CO_2H\cdot CH_2\cdot C{-}{-}{-}{-}N\end{array}\!\!>\!CH.$

0·75 Gram of 1-methyl-4-cyanomethylglyoxaline was dissolved in 20 c.c. of water, and boiled with 10 c.c. of 10 per cent. aqueous sodium hydroxide until no more ammonia was evolved. Then 9 c.c. of 10 per cent. hydrochloric acid were added, followed by 1·5 grams of picric acid in 40 c.c. of boiling water. On cooling, 1·5 grams of 1-*methylglyoxaline-4-acetic acid picrate* separated in large, striated prisms, melting at 187—189° (corr.), and a further 0·4 gram equally pure was obtained on concentrating the mother liquor, the yield thus amounting to 83 per cent. of the theoretical:

0·1209 gave 0·1751 CO_2 and 0·0332 H_2O. C = 39·5; H = 3·1.

$C_6H_8O_2N_2,C_6H_3O_7N_3$ requires C = 39·0; H = 3·0 per cent.

Ethyl 1-*Methylglyoxaline*-4-*acetate*, $C_4H_5N_2\cdot CH_2\cdot CO_2Et$.

Eight grams of 1-methyl-4-cyanomethylglyoxaline picrate were converted into the base, and this boiled for two hours with 50 c.c. of 15 per cent. absolute alcoholic hydrogen chloride, when ammonium chloride separated. The mixture was evaporated to dryness under diminished pressure, dissolved in water, mixed with sodium carbonate, and extracted with chloroform, when ethyl 1-methylglyoxaline-4-acetate was obtained as a brown oil. This was converted into the picrate, and purified by crystallisation from water, when 4·2 grams of the pure salt were obtained, that is, 46 per cent. of the theoretical.

Ethyl 1-*methylglyoxaline*-4-*acetate picrate* crystallises from water in long, yellow fibres, having the appearance of glass wool. It is very sparingly soluble in cold, but readily so in hot, water. It melts at 133—134° (corr.):

0·1092 * gave 0·1700 CO_2 and 0·0370 H_2O. C = 42·4; H = 3·8.

$C_8H_{12}O_2N_2,C_6H_3O_7N_3$ requires C = 42·3; H = 3·8 per cent.

1-*Methylglyoxaline*-5-*acetic Acid*, $\begin{array}{l} CO_2H\cdot CH_2\cdot C\cdot NMe \\ \qquad\qquad\quad\ \, \| \\ \qquad\qquad\quad CH\text{--}N \end{array}\!\!\gg CH$.

This compound was prepared by hydrolysis of its nitrile, and isolated as the *picrate*. This salt crystallises from water in beautiful, hexagonal plates, which melt at 180—181° (corr.), after sintering a few degrees earlier. It is anhydrous and sparingly soluble in cold, but readily so in hot, water:

0·1200 gave 0·1732 CO_2 and 0·0358 H_2O. C = 39·4; H = 3·3.

$C_6H_8O_2N_2,C_6H_3O_7N_3$ requires C = 39·0; H = 3·0 per cent.

Reduction of 1-*Methyl*-4-*cyanomethylglyoxaline*.

Seven grams of 1-methyl-4-cyanomethylglyoxaline were reduced by means of 10 grams of sodium and 100 c.c. of absolute alcohol. The reaction product was acidified with hydrochloric acid, made strongly alkaline with sodium carbonate, evaporated to dryness under diminished pressure, and the residue extracted with alcohol. The alcoholic extract was evaporated to dryness, and the residue extracted successively with ether, ethyl acetate, and absolute alcohol.

The ethereal extract amounted to 3·0 grams; it was dissolved

* Dried at 100°.

in water, and poured into a litre of warm 1 per cent. aqueous picric acid, when 6·6 grams of 1-*methyl*-4-β-*aminoethylglyoxaline dipicrate* separated in a pure state on cooling. The mother liquor was extracted with ether to remove free picric acid and evaporated to low bulk, when about 0·5 gram of a crude picrate, melting at about 140°, separated. After several crystallisations from water, a very small amount of 1:4-dimethylglyoxaline picrate was isolated from it, but was not obtained quite pure. This salt melted at 162—163° (corr.), the pure salt (Trans., 1910, **97**, 1819) melting at 167—168° (corr.) in the same bath, whilst a mixture of the two melted at 162—163° (corr.), and a mixture of this salt with 1:5-dimethylglyoxaline picrate at 135—140°.

The ethyl acetate extract afforded a further 1·3 grams of pure 1-methyl-4-β-aminoethylglyoxaline dipicrate, so that the total yield of this compound amounted to 7·9 grams, that is, 23 per cent. of the theoretical.

The absolute alcohol extract gave, with picric acid, at first an amorphous precipitate, but later a small quantity of 1-methylglyoxaline-4-acetic acid picrate.

1-*Methyl*-4-β-*aminoethylglyoxaline*,

$$NH_2\cdot CH_2\cdot CH_2\cdot \overset{\displaystyle CH\cdot NMe}{\underset{\displaystyle}{\overset{\|}{C}}}\text{———}N \gt CH.$$

The *dipicrate* crystallises from water in large, flat needles, which melt at 217° (corr.). It is very sparingly soluble in cold water, and is anhydrous:

0·1803 gave 0·2468 CO_2 and 0·0498 H_2O. C = 37·3; H = 3·1.

$C_6H_{11}N_3,(C_6H_3O_7N_3)_2$ requires C = 37·0; H = 2·9 per cent.

The *dihydrochloride* was prepared from the dipicrate by means of hydrochloric acid and ether. It crystallises from absolute alcohol in colourless prisms, which melt at 204—206° (corr.), after drying at 100°. It is deliquescent, and readily soluble in water, but sparingly so in absolute alcohol:

0·1186 * gave 0·1596 CO_2 and 0·0708 H_2O. C = 36·7; H = 6·7.

$C_6H_{11}N_3,2HCl$ requires C = 36·4; H = 6·6 per cent.

Reduction of 1-*Methyl*-5-*cyanomethylglyoxaline. Formation of* 1-*Methyl*-5-β-*aminoethylglyoxaline.*

Three grams of 1-methyl-5-cyanomethylglyoxaline were reduced by means of sodium and alcohol, and the products worked up as in the case of the 1:4-compound.

The combined ethereal and ethyl acetate extracts gave first an amorphous picrate, then small quantities of 1-*methyl*-5-β-*amino-*

ethylglyoxaline dipicrate, which formed yellow needles, melting at 201° (corr.), after drying at 100°:

0·1181 * gave 0·1615 CO_2 and 0·0305 H_2O. C=37·3; H=2·9.

$C_6H_{11}N_3,(C_6H_3O_7N_3)_2$ requires C=37·0; H=2·9 per cent.

The mother liquor from this salt then gave a small quantity of 1: 5-dimethylglyoxaline picrate in clusters of slender needles, melting at 167—168° (corr.):

0·0907 gave 0·1345 CO_2 and 0·0267 H_2O. C=40·4; H=3·3.

$C_5H_8N_2,C_6H_3O_7N_3$ requires C=40·6; H=3·4 per cent.

This salt was identified by determination of the melting points of its mixtures with pure 1: 4- and 1: 5-dimethylglyoxaline picrates (Trans., 1910, **97**, 1819), when it was found that the mixture with the 1: 4-salt melted at 135—140°, whilst that with the 1: 5-salt still melted at 167—168° (corr.).

The alcoholic extract gave a very small quantity of a crystalline picrate which melted at 162—175°; it was probably impure 1-methylglyoxaline-5-acetic acid picrate, but the quantity obtained was insufficient for identification.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

CCXLVI.—*The Probable Cause of the Elimination of a Carbethoxyl Group as Ethyl Carbonate by the Action of Sodium Ethoxide.*

By FERDINAND BERNARD THOLE and JOCELYN FIELD THORPE.

SEVERAL instances have now been recorded in which the passage of an open-chair δ-cyanoethyl salt into an imino-derivative of *cyclo*pentane through the agency of cold alcoholic sodium ethoxide is accompanied by the elimination of a carbethoxy-group as ethyl carbonate. It is sufficient for our purpose to select two examples of this type of reaction from the recent experiments of Mitchell and Thorpe (Trans., 1910, **97**, 2261) on the formation of imino-derivatives of α-hydrindone. It was then shown that ethyl *o*-cyanobenzylmalonate (I) was transformed into ethyl 1-iminohydrindene-2-carboxylate (II), and that ethyl α-*o*-dicyano-β-phenylpropionate (III) was converted into 1-imino-2-cyanohydrindene (IV).

It was suggested that these and other reactions of the same kind

* Dried at 100°.

might be due to spatial conditions, and that, in the five-membered ring, the presence of two groups of large molecular volume attached

$$C_6H_4{<}\begin{matrix}CN\\ CH_2\cdot CH(CO_2Et)_2\end{matrix} + EtOH \longrightarrow$$

(I.)

$$C_6H_4{<}\begin{matrix}C(:NH)\\ CH_2\text{——}\end{matrix}{>}CH\cdot CO_2Et + CO(OEt)_2$$

(II.)

$$C_6H_4{<}\begin{matrix}CN\\ CH_2\cdot CH(CN)\cdot CO_2Et\end{matrix} + EtOH \longrightarrow$$

(III.)

$$C_6H_4{<}\begin{matrix}C(:NH)\\ CH_2\text{——}\end{matrix}{>}CH\cdot CN + CO(OEt)_2$$

(IV.)

to any one carbon atom might not be a condition of stability, and consequently, when the compound was treated by a suitable reagent, one of these groups was eliminated.

An examination of the facts shows that several derivatives of the five-carbon ring are known which have more than one carbethoxyl group attached to any one carbon atom, such as, for example, ethyl *cyclo*pentane-1 : 1 : 3 : 3-tetracarboxylate (V) and ethyl hydrindene-2 : 2-dicarboxylate (VI):

$$\begin{matrix}CH_2\cdot C(CO_2Et)_2\\ |\\ CH_2\cdot C(CO_2Et)_2\end{matrix}{>}CH_2 \qquad C_6H_4{<}\begin{matrix}CH_2\\ CH_2\end{matrix}{>}C(CO_2Et)_2$$

(V.) (VI.)

If our hypothesis is correct, these compounds should pass, on treatment with sodium ethoxide, into ethyl carbonate and the corresponding ethyl esters, thus:

$$\begin{matrix}CH_2\cdot C(CO_2Et)_2\\ |\\ CH_2\cdot C(CO_2Et)_2\end{matrix}{>}CH_2 + 2EtOH \longrightarrow$$

$$\begin{matrix}CH_2\cdot CH(CO_2Et)\\ |\\ CH_2\cdot CH(CO_2Et)\end{matrix}{>}CH_2 + 2CO(OEt)_2$$

and

$$C_6H_4{<}\begin{matrix}CH_2\\ CH_2\end{matrix}{>}C(CO_2Et)_2 + EtOH \longrightarrow$$

$$C_6H_4{<}\begin{matrix}CH_2\\ CH_2\end{matrix}{>}CH\cdot CO_2Et + CO(OEt)_2.$$

We have therefore prepared these compounds, the former by Pospischill's method (*Ber.*, 1898, **31**, 1950) from the disodium derivative of ethyl butanetetracarboxylate by the action of methylene iodide, and the latter by v. Baeyer and Perkin's method (*Ber.*, 1884, **17**, 122) from *o*-xylylene dibromide and ethyl sodiomalonate.

We find that both these esters are quite unacted on by cold alcoholic sodium ethoxide. It is evident, therefore, that the

influences causing the elimination of the carbethoxyl group prior to the formation of the five-ring imino-compounds cannot be ascribed to spatial conditions or to the over-weighting of any one carbon atom of the ring. A careful review of the facts showed, moreover, that the displacement of the carbethoxy-group by sodium in the manner illustrated by the equation:

$$C_6H_4{<}{}^{CN}_{CH_2\cdot CH(CO_2Et)_2} \longrightarrow C_6H_4{<}{}^{C(:NH)}_{CH_2\text{——}}{>}C(CO_2Et)_2 + NaOEt \longrightarrow$$

$$C_6H_4{<}{}^{C(:NH)}_{CH_2\text{——}}{>}CNa\cdot CO_2Et + CO(OEt)_2$$

could not be the determining cause of this reaction, because, *inter alia*, ethyl 1-iminohydrindene-2-carboxylate (II) and analogously constituted compounds do not react with sodium ethoxide to form sodium derivatives. Finally, we decided to compare the various classes of compounds in which this reaction had been noticed, and ultimately arrived at an explanation, which forms the subject of the present communication.

During some experiments on the constitution of glutaconic acid (Trans., 1905, **87**, 1681) it was found that ethyl α-cyano-αβγ-trimethylglutaconate (VII) when treated with sodium ethoxide was converted into ethyl α-cyano-αβγ-trimethylcrotonate (VIII) and ethyl carbonate, thus:

$$\underset{\text{(VII.)}}{CO_2Et\cdot CMe{:}CMe\cdot CMe(CN)\cdot CO_2Et} + EtOH \longrightarrow$$

$$\underset{\text{(VIII.)}}{CO_2Et\cdot CMe{:}CMe\cdot CHMe\cdot CN} + CO(OEt)_2.$$

A comparison of ethyl α-cyano-αβγ-trimethylglutaconate (VII) with the normal ring-compound from ethyl *o*-cyanobenzylmalonate (I*a*) shows that these substances have one important point in common, namely, that it is necessary for each of them to part with the carbethoxyl group before the hydrogen atom necessary to permit the substance to react in its tautomeric form can be acquired, thus:

$$\underset{\text{(I}a\text{.)}}{C_6H_4{<}{}^{C(:NH)}_{CH_2\text{——}}{>}C(CO_2Et)_2} \longrightarrow \begin{matrix} C_6H_4{<}{}^{C(:NH)}_{CH_2\text{——}}{>}CH\cdot CO_2Et \\ C_6H_4{<}{}^{C(NH_2)}_{CH_2\text{——}}{>}C\cdot CO_2Et \\ \text{(Tautomeric forms.)} \end{matrix}$$

$$\underset{\text{(VII.)}}{CO_2Et\cdot CMe{:}CMe\cdot CMe(CN)\cdot CO_2Et} \longrightarrow \begin{matrix} CO_2Et\cdot CMe{:}CMe\cdot CHMe\cdot CN \\ CO_2Et\cdot CHMe\cdot CMe{:}CMe\cdot CN \\ \text{(Tautomeric forms.)} \end{matrix}$$

This view at once suggests a close relationship between compounds having the complex HC·C:C and those, such as the imino-compounds, which have the complex HC·C:NH, and leads to the

general conclusion that when the terminal hydrogen atoms in systems of this type are all replaced, the tendency for the compound to acquire that hydrogen atom which is necessary to enable it to react in its tautomeric form is such that any group capable of replacement by hydrogen is at once eliminated in the presence of a suitable reagent.

In the next communication several instances are recorded in which this reaction has been employed for the preparation of substituted glutaconic acids. These examples clearly prove that when the mobile hydrogen atoms in derivatives of glutaconic acid are replaced, the tendency for the compound to acquire the mobile atom causes it to eliminate one carboxyl group as ethyl carbonate when it is treated with alcoholic sodium ethoxide.

Experimental.

Ethyl Hydrindene-2:2-dicarboxylate,

$$C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>C(CO_2Et)_2.$$

This substance was originally prepared by v. Baeyer and Perkin (*Ber.*, 1884, **17**, 122) by the condensation of *o*-xylylene dibromide and the sodium compound of ethyl malonate. It was, however, hydrolysed to the acid without further purification. The method of preparation used by us was the same as that employed by these chemists, but we find that the ester boils at 186°/19 mm., and that it sets to a crystalline mass on cooling. When recrystallised from a small quantity of alcohol it is obtained in long needles, which melt at 38°:

0·2030 gave 0·5092 CO_2 and 0·1272 H_2O. C = 68·81; H = 6·92.

$C_{15}H_{18}O_4$ requires C = 68·7; H = 6·9 per cent.

The ester is quite unaltered by sodium ethoxide.

Ethyl cyclo*Pentane-1:1:3:3-tetracarboxylate,*

$$\begin{matrix}CH_2\cdot C(CO_2Et)_2\\|\\CH_2\cdot C(CO_2Et)_2\end{matrix}>CH_2.$$

This substance was prepared by Pospischill's method (*Ber.*, 1898, **31**, 1950) from ethyl butanetetracarboxylate,

$$(CO_2Et)_2CH\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2,$$

which was obtained both by the condensation of ethylene dibromide and ethyl sodiomalonate and by the condensation of ethyl *cyclo*propane-1:1-dicarboxylate, which is also formed in this action, with a further quantity of the sodium compound of ethyl malonate. The desired ester was obtained by condensing ethyl butanetetracarboxylate with methylene iodide. We find that it can be distilled

under 15 mm. pressure when small quantities are employed, and boils at 225—227°:

0·2013 gave 0·4201 CO_2 and 0·1342 H_2O. C=56·93; H=7·41.

$C_{17}H_{26}O_8$ requires C=57·0; H=7·3 per cent.

The ester was treated with two atomic proportions of sodium dissolved in alcohol, but was recovered unchanged.

THE SORBY RESEARCH LABORATORY,
THE UNIVERSITY, SHEFFIELD.

CCXLVII.—*The Chemistry of the Glutaconic Acids. Part I. Methods for the Preparation of the Alkylglutaconic Acids which Prove the Identity of the α- and γ-Positions in the Glutaconic Acid Molecule.**

By FERDINAND BERNARD THOLE and JOCELYN FIELD THORPE.

SOME years ago one of us, in conjunction with H. Rogerson (Trans., 1905, **87**, 1669, 1685), published a new method by which alkyl derivatives of glutaconic acid, having a methyl group in the β-position, and any desired alkyl group in either the α- or γ-position, or in both of these, could be prepared in quantity. The method involved the condensation of the sodium derivative of ethyl cyanoacetate with ethyl acetoacetate, when a reaction occurred which is expressed by the equation:

$$CO_2Et\cdot CHNa\cdot CN + HO\cdot CMe\colon CH\cdot CO_2Et \longrightarrow CO_2Et\cdot CNa(CN)\cdot CMe\colon CH\cdot CO_2Et + H_2O.$$

By heating this sodium derivative, or, better, the potassium compound, with alkyl iodides, the corresponding alkyl derivatives were produced, and these, when further treated with sodium ethoxide and an alkyl iodide, yielded the trialkylated esters, thus:

$$CO_2Et\cdot CR(CN)\cdot CMe\colon CNa\cdot CO_2Et + RI \longrightarrow CO_2Et\cdot CR(CN)\cdot CMe\colon CR\cdot CO_2Et.$$

An important feature of this reaction is that the hydrogen of the complex $\colon CH\cdot CO_2Et$, which is present in the dialkylated ester, is readily displaced by sodium. This is contrary to the conclusion arrived at by Blaise (*Bull. Soc. chim.*, 1903, [iii], **29**, 1016; *Compt. rend.*, 1903, **136**, 381, 692, 1140), who found that only those

* For the abstract of this paper see Proc., 1911, **27**, 122.

derivatives of glutaconic ester which contain the complex $\dot{:}C{\cdot}CHX{\cdot}$ react with sodium ethoxide. Now it is certain that compounds having this structure react in this manner, a fact which is clearly proved, not only by the work of Henrich (*Monatsh.*, 1899, **20**, 560), who discovered this reaction by preparing *αα*-dimethylglutaconic acid from the product of the methylation of ethyl glutaconate,

$$CO_2Et{\cdot}CH_2{\cdot}CH\dot{:}CH{\cdot}CO_2Et \longrightarrow CO_2Et{\cdot}CMe_2{\cdot}CH\dot{:}CH{\cdot}CO_2Et.$$

but also by the subsequent work of Perkin and Smith (Trans., 1903, **83**, 8) and of Blaise (*loc. cit.*). It is, however, also certain that the property of this complex of yielding a sodium compound is entirely determined by the tendency of the mobile hydrogen atom present in the glutaconic acid derivative to pass outside the three-carbon system to the neighbouring carbonyl group. Thus the sodium compounds of this type are always yellow, and there is no doubt that they possess a structure represented by the expression $\cdot C\dot{:}C{\cdot}C\dot{:}C(ONa){\cdot}OEt$. Abundant proof will be given in this and in the subsequent papers of this series showing that the property of glutaconic acid derivatives of forming compounds of this type diminishes with the increase of alkyl groups in the molecule, and thus the trialkyl derivatives, $CN{\cdot}CHMe{\cdot}CMe\dot{:}CMe{\cdot}CO_2Et$ and $CO_2Et{\cdot}CHMe{\cdot}CMe\dot{:}CMe{\cdot}CO_2Et$, do not form sodium derivatives with sodium ethoxide (Trans., 1905, **87**, 1702, 1706). It has also been shown by Feist and Beyer (*Annalen*, 1906, **345**, 117) that the introduction of a methyl group into the ester $CO_2Et{\cdot}CHMe{\cdot}CMe\dot{:}CH{\cdot}CO_2Et$ (or $CO_2Et{\cdot}CH_2{\cdot}CMe\dot{:}CMe{\cdot}CO_2Et$) cannot be effected by the aid of sodium ethoxide and methyl iodide. It therefore follows that in the absence of the mobile hydrogen atom, and possibly, also, owing to the presence of negative groups on the more remote carbon atom, the hydrogen atom of the complex $\dot{:}CHX$ is displaceable by sodium, but such sodium compounds are without colour, and presumably have the metal attached to carbon.

The chief proof of the virtual tautomerism of the glutaconic acid molecule advanced in the former paper rested on the structure of two esters (I and II):

$$\underset{\text{(I.)}}{CO_2Et{\cdot}CMe(CN){\cdot}CMe\dot{:}CH{\cdot}CO_2Et.}$$

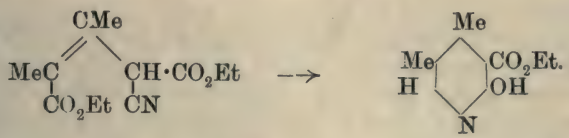
$$\underset{\text{(II.)}}{CO_2Et{\cdot}CH(CN){\cdot}CMe\dot{:}CMe{\cdot}CO_2Et.}$$

Ester (I) was prepared by the condensation of the potassium compound, to which we assigned the constitution

$$CO_2Et{\cdot}CK(CN){\cdot}CMe\dot{:}CH{\cdot}CO_2Et,$$

with methyl iodide. Ester (II) was prepared by the condensation

of ethyl sodiocyanoacetate and ethyl methylacetoacetate. The structure of these two esters was shown to be different by the transformation of (II) into a derivative of dihydroxypyridine by the action of concentrated sulphuric acid, thus:



whereas (I) remained unacted on under the same experimental conditions.

From the fact that esters (I) and (II) yielded the same dimethylglutaconic acid on hydrolysis, it was concluded that the molecule of glutaconic acid is symmetrical, and that the α- and γ-positions in this substance are identical. It was also shown that β-methyl-α-ethylglutaconic acid, $CO_2H\cdot CHEt\cdot CMe\colon CH\cdot CO_2H$, and β-methyl-γ-ethylglutaconic acid, $CO_2H\cdot CEt\colon CMe\cdot CH_2\cdot CO_2H$, prepared by a similar method were also identical. Since that time the correctness of this conclusion has not been generally accepted, and it has been suggested (Meyer and Jacobson, "Lehrbuch der Organischen Chemie," 1910, 2te Aufl, I, ii, 440) that, during the process of the hydrolysis, the bond must have shifted in either one case or the other, thus yielding the same acid. This point was fully discussed at the time, but was discarded as highly improbable.

It is unfortunate that the real issue, namely, the identity of the α- and γ-positions, should have been masked in the previous paper by the mis-statement that only those derivatives of glutaconic acid which have the mobile hydrogen atom substituted can exist in two modifications. This error was quickly corrected by Feist (*Annalen*, 1906, **345**, 77), who pointed out that β-methylglutaconic acid, $CO_2H\cdot CH_2\cdot CMe\colon CH\cdot CO_2H$, had already been prepared in two well-defined modifications, a fact which had escaped our notice.

Since then, Feist (*Annalen*, 1909, **370**, 41) and Feist and Pomme (*ibid.*, 61) have shown that α-methylglutaconic acid,

$$CO_2H\cdot CHMe\cdot CH\colon CH\cdot CO_2H,$$

can be isolated in two modifications, but that the *cis*-form is relatively unstable. It is therefore evident that, if our view of the constitution of glutaconic acid is correct, the occurrence of stereoisomeric forms must be independent of the mobile hydrogen atom, and it therefore seemed to us desirable to institute a series of experiments on the chemistry of these substances. In the present paper we shall show:

(1) That the α-alkylglutaconic acids, $CO_2H\cdot CHR\cdot CH\colon CH\cdot CO_2H$,

and the γ-alkylglutaconic acids, $CO_2H{\cdot}CH_2{\cdot}CH{:}CR{\cdot}CO_2H$, are the same substances, and that α-methyl-γ-ethylglutaconic acid,

$$CO_2H{\cdot}CHMe{\cdot}CH{:}CEt{\cdot}CO_2H,$$

and γ-methyl-α-ethylglutaconic acid, $CO_2H{\cdot}CHEt{\cdot}CH{:}CMe{\cdot}CO_2H$, are identical.

(2) That the stability of the *cis*-forms of the α-substituted acids increases with the molecular weight of the substituting group.

It is probable that the cause of the identity of the α- and γ-positions is of the same order as that determining the equality of the meta-positions in the benzene ring, and in the ensuing papers we propose to write the formulæ of these substances thus:

$$CO_2H{\cdot}CH{\cdot}CH(\mathbf{H}){\cdot}CH{\cdot}CO_2H,$$

indicating the mobile hydrogen atom by means of heavy type, but we have retained the older formulæ in the introduction for the sake of clearness.

At the same time it is necessary to offer some explanation respecting the cause of the existence of stereoisomerism among certain members of this series, because it is evident that the presence of the mobile hydrogen atom must prevent the occurrence of isomerism corresponding with maleic and fumaric acids. The explanation we suggest is as follows: The stereoisomerism of all acids of the type $CO_2H{\cdot}CR_2{\cdot}CH{:}CH{\cdot}CO_2H$, in which the mobile hydrogen atom is displaced, has been clearly established, and there is no doubt that this isomerism is represented by the formulæ:

$$\begin{array}{r} CO_2H{\cdot}CH \\ \| \\ CO_2H{\cdot}CR_2{\cdot}CH \end{array} \qquad\qquad \begin{array}{l} CO_2H{\cdot}CH \\ \qquad\quad\ \| \\ \qquad\quad CH{\cdot}CR_2{\cdot}CO_2H \end{array}$$

cis-(Maleic)-form. *trans*-(Fumaric)-form.

Of the acids containing the mobile hydrogen atom, β-methylglutaconic acid, $CO_2H{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CO_2H$, exists in two well-defined forms, and Feist has shown that α-methylglutaconic acid, $CO_2H{\cdot}CHMe{\cdot}CH{:}CH{\cdot}CO_2H$, can be isolated in a *cis*-modification melting at 118°, which is relatively unstable, and can only be formed from the anhydride in the presence of casein. In the present paper we show that *cis*-α-ethylglutaconic acid and *cis*-α-benzylglutaconic acid are stable substances. In spite of numerous attempts we have not yet succeeded in isolating any other of the "mobile" alkylglutaconic acids in two modifications, but we agree with Feist that such forms must be capable of existence, but are difficult to isolate owing to their instability. It is considered that the so-called stereoisomerism of these acids is in reality structural isomerism, and is a property depending on a difference in structure of the carboxyl groups. It is proposed to deal fully with this question in Part IV. of this series, but the terms

cis- and *trans-* are retained in this and the succeeding paper for the sake of clearness.

Preparation of the Alkylglutaconic Acids.

The preparation of alkyl derivatives of glutaconic acids having a methyl group in the β-position has already been described; the preparation in quantity of alkylglutaconic acids having this position unoccupied was a problem which had to be solved.

The α-substituted derivatives can be readily prepared by the alkylation of the yellow sodium compound which Conrad and Guthzeit (*Annalen*, 1883, **222**, 259) prepared by the action of chloroform on the sodium compound of ethyl malonate:

$$(CO_2Et)_2CNa\cdot CH\dot{:}C(CO_2Et)_2 + RI \longrightarrow (CO_2Et)_2CR\cdot CH\dot{:}C(CO_2Et)_2 + NaI;$$

but the preparation of further alkylated products is a matter of some difficulty. (For a description of these methods compare Feist, *Annalen*, 1909, **370**, 41).

We ultimately devised a method for the preparation of these acids which rests upon an observation recorded in the previous paper (Trans., 1905, **77**, 1702), namely, that ethyl α-cyano-$\alpha\beta\gamma$-trimethylglutaconate readily passes into ethyl carbonate and ethyl γ-cyano-$\alpha\beta\gamma$-trimethylcrotonate when it is treated with cold sodium ethoxide, thus:

$$CO_2Et\cdot CMe(CN)\cdot CMe\dot{:}CMe\cdot CO_2Et + EtOH \longrightarrow CHMe(CN)\cdot CMe\dot{:}CMe\cdot CO_2Et + CO(OEt)_2.$$

This reaction suggested the general principle that when the mobile hydrogen atoms in compounds of the type of glutaconic ester are all displaced the tendency for the compound to acquire the hydrogen atom necessary for tautomerism is such that the element is at once introduced in the presence of a suitable reagent.

The alkyl derivatives prepared by the action of an alkyl iodide on Conrad and Guthzeit's yellow sodium compound are of this type, and should therefore react with cold sodium ethoxide, thus:

$$(CO_2Et)_2CR\cdot CH\dot{:}C(CO_2Et)_2 + EtOH \longrightarrow CO_2Et\cdot CHR\cdot CH\dot{:}C(CO_2Et)_2 + CO(OEt)_2.$$

Experiment showed that this reaction proceeded quantitatively, but that in the presence of sodium ethoxide the metal passed to the most negative carbon atom, yielding a sodium compound of the formula *:

$$CO_2Et\cdot CR\dot{:}CH\cdot CNa(CO_2Et)_2.$$

* The sodium compounds, which are deep yellow, are written in this form for the sake of clearness, although they have undoubtedly the enolic formulæ assigned to them by Henrich (*Annalen*, 1910, **376**, 122).

This was proved by treating the sodium compound, when R = Me, with methyl iodide, when the product on hydrolysis yielded Reformatzky's $\alpha\gamma$-dimethylglutaconic acid,

$$CO_2H\cdot CHMe\cdot CH\dot{:}CMe\cdot CO_2H,$$

unaccompanied by any other acid.

The speed of the reaction varies with the value of R; thus when R = methyl the change from the tetraethyl to the triethyl ester is complete in the course of an hour at the ordinary temperature. When R = ethyl, two to two and a-half hours are required, and when R = benzyl the reaction takes at least twelve hours before the transformation is completely effected.

When the above sodium compound is treated with an alkyl iodide the ester $CO_2Et\cdot CR\dot{:}CH\cdot CR(CO_2Et)_2$ is formed; this is another instance of a glutaconic ester in which the mobile hydrogen atoms are displaced.

It should therefore react with cold sodium ethoxide, thus:

$$CO_2Et\cdot CR\dot{:}CH\cdot CR(CO_2Et)_2 + EtOH \longrightarrow CO_2Et\cdot CR\dot{:}CH\cdot CHR\cdot CO_2Et + CO(OEt)_2.$$

This reaction also proceeds quantitatively, but here again the time varies with the value of R. It is not possible to eliminate more than one carbethoxy-group from an alkyl derivative of ethyl dicarbethoxyglutaconate or similarly constituted ethyl ester, even by using two equivalent proportions of sodium ethoxide; thus ethyl $\alpha\gamma$-dicarbethoxy-α-methylglutaconate when left for several hours in contact with twice the quantity necessary to eliminate one carbethoxy-group yields only the triethyl ester, thus:

$$(CO_2Et)_2CMe\cdot CH\dot{:}C(CO_2Et)_2 \longrightarrow CO_2Et\cdot CHMe\cdot CH\dot{:}C(CO_2Et)_2.$$

It is evident that this is caused by the production of the sodium compound, $CO_2Et\cdot CMe\dot{:}CH\cdot C(CO_2Et)\dot{:}C(ONa)\cdot OEt$, and the elimination of a further carbethoxy-group from this substance would not supply the hydrogen atom necessary for virtual tautomerism.

It is therefore necessary in all these reactions to have one molecular proportion of sodium ethoxide present. If, however, the product does not form a sodium derivative, or forms a derivative which is dissociated by alcohol, then the change is effected by the aid of a trace of sodium ethoxide; thus the reaction:

$$CO_2Et\cdot CMe(CN)\cdot CMe\dot{:}CMe\cdot CO_2Et + EtOH \longrightarrow CHMe(CN)\cdot CMe\dot{:}CMe\cdot CO_2Et + CO(OEt)_2,$$

can be brought to completion in the presence of one-tenth the molecular quantity of sodium ethoxide. By this means, therefore, we had at our disposal a method by which any alkyl derivative of glutaconic acid substituted in either the α- or γ-positions or in both of them by any desired alkyl group could be prepared in

quantity, and we then proceeded to gain fresh evidence of the identity of the α- and γ-positions in the glutaconic acid molecule.

The Identity of α- and γ-Alkylglutaconic Acids.

α-Methylglutaconic acid is prepared by the hydrolysis of the ester $(CO_2Et)_2CMe\cdot CH\colon C(CO_2Et)_2$, and we satisfied ourselves that the same acid, unaccompanied by any other modification, was formed from this ester, both by acid and alkaline hydrolysis.

The action of sodium ethoxide on the ester produces, as already mentioned, a sodium compound of the formula

$$CO_2Et\cdot CMe\colon CH\cdot CNa(CO_2Et)_2,$$

and the ester prepared from this sodium derivative by the action of acids should on hydrolysis yield γ-methylglutaconic acid,

$$CO_2H\cdot CMe\colon CH\cdot CH_2\cdot CO_2H.$$

Both by acid and alkaline hydrolysis the ester yields the already known α-methylglutaconic acid unaccompanied by any other substance. In order to place the identity of these positions beyond question, we prepared the sodium compound:

$$CO_2Na\cdot CMe\colon CH\cdot CNa(CO_2Na)_2,$$

from which was obtained the already known methylglutaconic acid. It is clear, therefore, that α-methyl- and γ-methyl-glutaconic acids are the same substance. In the same way it was shown that both α- and γ-ethylglutaconic acids and α- and γ-benzylglutaconic acids, respectively, are identical.

The Identity of α-Methyl-γ-ethylglutaconic Acid and γ-Methyl-α-ethylglutaconic Acid.

γ-Methyl-α-ethylglutaconic acid, $CO_2H\cdot CMe\colon CH\cdot CHEt\cdot CO_2H$, was prepared by the following series of reactions: Ethyl αγ-dicarbethoxy-α-methylglutaconate, $(CO_2Et)_2CMe\cdot CH\colon C(CO_2Et)_2$, was converted into the sodium compound, $CO_2Et\cdot CMe\colon CH\cdot CNa(CO_2Et)_2$, which on ethylation furnished the ethyl derivative,

$$CO_2Et\cdot CMe\colon CH\cdot CEt(CO_2Et)_2.$$

This ester was hydrolysed (1) through the sodium salt,

$$CO_2Na\cdot CMe\colon CH\cdot CEt(CO_2Na)_2,$$

and (2) through the compound $CO_2Et\cdot CMe\colon CH\cdot CHEt\cdot CO_2Et$ (see p. 2192). The methylethylglutaconic acid prepared by these two processes was the same substance; it must therefore be γ-methyl-α-ethylglutaconic acid, $CO_2H\cdot CMe\colon CH\cdot CHEt\cdot CO_2H$.

α-Methyl-γ-ethylglutaconic acid, $CO_2H\cdot CEt\colon CH\cdot CHMe\cdot CO_2H$, was prepared in the following way: The sodium derivative,

$$(CO_2Et)_2CNa\cdot CH\colon C(CO_2Et)_2,$$

on ethylation gave the ethyl compound,

$$(CO_2Et)_2CEt\cdot CH{:}C(CO_2Et)_2,$$

and this on treatment with sodium ethoxide yielded the sodium compound, $CO_2Et\cdot CEt{:}CH\cdot CNa(CO_2Et)_2$, which on methylation furnished the methyl compound, $CO_2Et\cdot CEt{:}CH\cdot CMe(CO_2Et)_2$.

As in the previous case, this ester was hydrolysed (1) through the sodium salt, $CO_2Na\cdot CEt{:}CH\cdot CMe(CO_2Na)_2$, and (2) through the compound $CO_2Et\cdot CEt{:}CH\cdot CHMe\cdot CO_2Et$ (see p. 2192). The same acid was produced by both these methods, and it must therefore be α-methyl-γ-ethylglutaconic acid,

$$CO_2H\cdot CEt{:}CH\cdot CHMe\cdot CO_2H.$$

γ-Methyl-α-ethylglutaconic acid and α-methyl-γ-ethylglutaconic acid prepared by these methods are the same compound.

During the course of these experiments it has been frequently noticed that the esters of substituted glutaconic acids tend to decompose during alkaline hydrolysis, yielding derivatives of malonic acid. A similar instance of this kind was recorded in a previous paper (Trans., 1905, **87**, 1693; compare also Claisen, *Annalen*, 1897, **297**, 89; Bolam, *Ber.*, 1894, **27**, 3061; Guthzeit and Bolam, *J. pr. Chem.*, 1896, [ii], **54**, 359), when it was found that ethyl α-cyano-β-methylglutaconate,

$$CO_2Et\cdot CH(CN)\cdot CMe{:}CH\cdot CO_2Et,$$

yielded some malonic acid when hydrolysed by alcoholic potassium hydroxide. In the present paper it is shown that the tendency for esters of this type to undergo fission appears to increase with the molecular weight of the groups present in the molecule; thus the ester $CO_2Et\cdot CHMe\cdot CH{:}C(CO_2Et)_2$ is hydrolysed completely to α-methylglutaconic acid, but, under the same conditions, the ester $CO_2Et\cdot CHEt\cdot CH{:}C(CO_2Et)_2$ yields a small quantity of ethylmalonic acid, whilst the ester $CO_2Et\cdot CH(CH_2Ph)\cdot CH{:}C(CO_2Et)_2$ yields benzylmalonic acid, the amount representing about 15 per cent. of the ester hydrolysed. This last reaction recalls the behaviour of benzaldehyde towards potassium hydroxide, and it is possible that the mechanism of these reactions involves the formation of the aldehyde, thus:

$$CO_2Et\cdot CHR\cdot CH{:}C(CO_2Et)_2 + H_2O \longrightarrow CO_2Et\cdot CHR\cdot CHO + CH_2(CO_2Et)_2.$$

It is significant that only those esters which contain a mobile hydrogen atom behave in this manner, and that the corresponding tetracarboxylic esters of the type $(CO_2Et)_2CR\cdot CH{:}C(CO_2Et)_2$ are hydrolysed directly to the acid without undergoing any disruption. It is of importance to remember this point when preparing the alkyl derivatives of glutaconic acid, because experiment shows that the best yield of acid is obtained from esters containing the mobile

hydrogen atom by hydrolysing them with acid hydrolysing agents, whereas the esters which have the mobile hydrogen atom displaced are best hydrolysed by alkaline hydroxides.

Guthzeit and Dressel have shown (*Ber.*, 1889, **22**, 1415) that when ethyl dicarbethoxyglutaconate is distilled under diminished pressure, alcohol is eliminated and ethyl 6-ethoxy-α-pyrone-3 : 5-dicarboxylate is formed, thus:

$$\begin{array}{lcl} CO_2Et\cdot \underset{|}{C}H\cdot CH{:}C(CO_2Et)_2 & \longrightarrow & CO_2Et\cdot \underset{|}{C}{:}CH\cdot C(CO_2Et){:}\underset{|}{C}\cdot OEt \\ \qquad\quad CO_2Et & & \qquad\quad CO_2Et \qquad\qquad\qquad OH \\ & \longrightarrow & CO_2Et\cdot \underset{|}{C}{:}CH\cdot C(CO_2Et){:}\underset{|}{C}\cdot OEt \\ & & \qquad\quad CO\text{------------------}O \end{array}$$

The formation of a pyrone derivative in this manner shows that in a compound of the type of ethyl dicarbethoxyglutaconate there is a considerable tendency for the mobile hydrogen atom to pass outside the three-carbon system, and, as a matter of fact, it is probable that this ester, which gives a marked coloration with ferric chloride, consists largely of the enolic form at the ordinary temperature.

It is shown in this and the succeeding papers that the tendency for the mobile hydrogen atom to pass outside the three-carbon system is mainly determined by the nature of the groups attached to the α-carbon atom, and it is therefore of interest to compare the properties of the corresponding triethyl esters, which also contain the mobile hydrogen atom, as regards their capacity for forming pyrone derivatives; thus ethyl carbethoxy-α-methylglutaconate, $CO_2Et\cdot CHMe\cdot CH{:}C(CO_2Et)_2$, gives no coloration with ferric chloride, and can be distilled without undergoing change. Ethyl carbethoxy-α-ethylglutaconate, $CO_2Et\cdot CHEt\cdot CH{:}C(CO_2Et)_2$, also gives no coloration with ferric chloride, and is likewise unaltered on distillation. Ethyl carbethoxy-α-benzylglutaconate,

$$CO_2Et\cdot CH(CH_2Ph)\cdot CH{:}C(CO_2Et)_2,$$

on the other hand, gives a marked coloration with ferric chloride, and when slowly distilled passes into ethyl 6-ethoxy-3-benzyl-α-pyrone 5-carboxylate, thus:

$$\begin{array}{lcl} CH_2Ph\cdot \underset{|}{C}H\cdot CH{:}C(CO_2Et)_2 & \longrightarrow & CH_2Ph\cdot \underset{|}{C}{:}CH\cdot C(CO_2Et){:}\underset{|}{C}\cdot OEt \\ \qquad\quad CO_2Et & & \qquad\quad CO_2Et \qquad\qquad\qquad OH \\ & \longrightarrow & CH_2Ph\cdot \underset{|}{C}{:}CH\cdot C(CO_2Et){:}\underset{|}{C}\cdot OEt \\ & & \qquad\quad CO\text{------------------}O \end{array}$$

So far, this is the only triethyl ester of the series which we have succeeded in transforming into the pyrone ring, and it is evident that the presence of a large group attached to the α-carbon atom is necessary in order to displace the mobile hydrogen atom from

the three-carbon system. The dicarboxylic esters of the series are quite unaltered on distillation.

Experimental.

Ethyl $\alpha\gamma$-*Dicarbethoxy*-α-*methylglutaconate*, $(CO_2Et)_2CMe\cdot CH{:}C(CO_2Et)_2$.

The methylation of the yellow sodium compound of ethyl dicarbethoxyglutaconate was effected by Conrad and Guthzeit (*Annalen*, 1883, **222**, 259), who employed the action of alcoholic methyl iodide in sealed tubes at a high temperature for this purpose. Ruhemann (Trans., 1893, **63**, 880) found that the presence of alcohol led to unsatisfactory results, and therefore heated the yellow sodium compound to a high temperature with methyl iodide alone. Feist and Pomme (*Annalen*, 1909, **370**, 63), who succeeded in isolating the two stereoisomeric forms of α-methylglutaconic acid, prepared the acid of higher melting point by hydrolysing the above methyl derivative, which they prepared by the action of alcoholic methyl sulphate on the yellow sodium derivative.

The first two methods of preparation are tedious, and so far as the last-named process is concerned we were quite unable to reproduce the conditions given by Feist and Pomme in their paper. In our hands the action of methyl sulphate yielded hardly 10 per cent. of the methyl derivative, the remainder of the product comprising unaltered ethyl dicarbethoxyglutaconate,* together with ethyl 6-ethoxy-α-pyrone-3:5-dicarboxylate, melting at 94°, a substance which Guthzeit and Dressel (*Ber.*, 1889, **22**, 1415) have prepared previously. Ultimately we found that the best way to prepare ethyl dicarbethoxy-α-methylglutaconate is merely to heat a solution of the yellow sodium compound (50 grams) in alcohol (120 grams) with methyl iodide (30 grams) on the water-bath for five hours. The colourless solution was poured into water and extracted by ether; the ethereal extract, after being washed with water and shaken with a 10 per cent. solution of potassium hydroxide until the extract ceased to be yellow, was dried and evaporated. The residual oil yielded on distillation 40 grams of pure ethyl dicarbethoxy-α-methylglutaconate, boiling at 211°/21 mm., that is, 83 per cent. of the theoretical amount. (Found, C = 55·71; H = 7·02. Calc., C = 55·8; H = 7·0 per cent.)

Hydrolysis.—Ten grams of the ethyl salt were boiled with dilute hydrochloric acid until completely hydrolysed, when the liquid was evaporated to a small bulk and allowed to crystallise. The acid

* The yellow colour of the sodium compound is entirely discharged in this experiment. The reaction is therefore complete.

is best prepared, however, by hydrolysis with an alcoholic solution containing one and a-half times the calculated quantity of potassium hydroxide, when the clear solution of the potassium salt, which evolves carbon dioxide on acidification, yields the pure acid on extraction by ether. Owing to the insolubility of α-methylglutaconic acid in dry ether, the acid separates in a very pure condition when the dried ethereal solution is evaporated to a small bulk. By both these methods the already known α-methylglutaconic acid melting at 145—146° was obtained, unaccompanied by any other substance. (Found, C=49·84; H=5·70. Calc., C=50·0; H=5·6 per cent.)

Ethyl Carbethoxy-α-methylglutaconate, $CO_2Et{\cdot}CMe{\cdot}CH(H){\cdot}C(CO_2Et)_2$.

The elimination of one carbethoxy-group from ethyl dicarbethoxy-α-methylglutaconate was effected as follows: Forty grams of the tetraethyl ester dissolved in 30 c.c. of alcohol were mixed with a solution containing 2·8 grams of sodium in 32 c.c. of alcohol. The solution became warm and deep yellow, whilst the characteristic odour, which always accompanies the production of ethyl carbonate in these reactions, was at once apparent. After an hour the mixture was poured into dilute hydrochloric acid, and the oil extracted by ether. The ethereal extract after being washed was shaken with a little dilute alkali, dried, and evaporated. The residual oil was then distilled under ordinary pressure until the thermometer registered 140°, when the operation was continued under diminished pressure. The triethyl ester distilled at 182°/22 mm. as a colourless oil without appreciable odour. Yield, 28 grams, or 93 per cent. of the theoretical:

0·2311 gave 0·4838 CO_2 and 0·1505 H_2O. C=57·10; H=7·25.

$C_{13}H_{20}O_6$ requires C=57·3; H=7·4 per cent.

The substance gives no colour with ferric chloride.

The less volatile portion was fractionated under the ordinary pressure, and the large fraction, which boiled at 126°, was characterised as ethyl carbonate by analysis. (Found, C=50·58; H=8·50. Calc., C=50·8; H=8·5 per cent.)

α(or γ)-*Methylglutaconic Acid*, $CO_2H{\cdot}CMe{\cdot}CH(H){\cdot}CH{\cdot}CO_2H$.

Ethyl carbethoxy-α-methylglutaconate was subjected to the hydrolysing action of both acids and alkalis in order to prove that α- and γ-methylglutaconic acids were the same substance (compare p. 2193).

Acid Hydrolysis.—The ester was boiled with ten times its bulk of 10 per cent. hydrochloric acid until all had passed into solution, when the product was evaporated to half its volume, and the acid allowed to crystallise. The crude acid melted at 143—146°, and when recrystallised from water melted at 145—146°. The filtrate from the crude acid gave on evaporation an acid which melted at 142—144°, and it is therefore evident that no other substance is formed during the hydrolysis. The acid was proved to be the already known α-methylglutaconic acid by direct comparison with the acid prepared as described on p. 2197.

Alkaline Hydrolysis: Formation of the Sodium Salt,
$CO_2Na{\cdot}CMe{:}CH{\cdot}CNa(CO_2Na)_2$.

—Twenty-six grams of the ester were added to a solution containing 8·4 grams of sodium dissolved in alcohol, to which 25 c.c. of water had been added. The whole was then warmed on the water-bath, when the yellow solution gradually deposited a white precipitate of the sodium salt. This was collected and washed with alcohol until quite colourless, when it was spread on a porous plate and dried at 80°:

0·4137 gave 0·4443 Na_2SO_4. Na = 33·15.

$C_7H_4O_6Na_4$ requires Na = 33·3 per cent.

The sodium salt was dissolved in ice-cold water, and cautiously acidified by the addition of the calculated quantity of hydrochloric acid. The strongly alkaline solution which the salt forms with water effervesced freely on the addition of the acid, and when all carbon dioxide had been evolved the solution was extracted by ether. The dried ethereal solution when evaporated yielded a solid acid, which melted at 133—140°. This was then rubbed with dry ether, in which it was very sparingly soluble, and yielded an acid melting at 145—146°. The identity of this acid with α-methylglutaconic acid was proved (1) by a mixed melting-point determination, (2) by the formation of the characteristic chloro-anhydride (see Part II). (Found, C = 49·88; H = 5·68. Calc., C = 50·0; H = 5·6 per cent.).

The small quantity of acid which remained on evaporating the ethereal washings from the purification of the above acid melted at 125—133°; when rubbed with a little dry ether this yielded a further quantity of the acid, melting at 145—146°. The ultimate residue, which did not weigh more than 0·5 gram, remained viscid even after some weeks. It possibly contained some of Feist's *cis*-modification melting at 118°, but we were unable to isolate any pure substance from it.

Ethyl $\alpha\gamma$*-Dicarbethoxy-*α*-ethylglutaconate,*
$(CO_2Et)_2CEt\cdot CH{:}C(CO_2Et)_2$.

As in the case of the corresponding methyl derivative, we found that by far the best way to prepare this compound is to heat an alcoholic solution of the yellow sodium compound together with excess of ethyl iodide on the water-bath for twenty-four hours. The product was worked up as described for the methyl derivative (p. 2197). The oil obtained boiled at 213°/20 mm.; yield, 80 per cent. of the theoretical. (Found, C = 56·89; H = 7·06. Calc., C = 57·0; H = 7·3 per cent.)

Ethyl Carbethoxy-α*-ethylglutaconate,*
$CO_2Et\cdot CEt\cdot CH(H)\cdot C(CO_2Et)_2$.

This substance was prepared by the action of cold alcoholic sodium ethoxide on ethyl dicarbethoxy-α-ethylglutaconate, but the reaction requires a longer time than is the case with the corresponding methyl derivative.

Thirty-one grams of the ethyl salt dissolved in 25 c.c. of alcohol were added to a solution containing 2 grams of sodium dissolved in 25 c.c. of alcohol. The mixture became warm and deep yellow, but the heat developed was not so great as with the methyl derivative. After three hours at the ordinary temperature the mixture was poured into dilute hydrochloric acid, and the oil extracted by ether. The residual liquid was then fractionated, and the fraction boiling at 180°/20 mm. collected. Yield, 95 per cent. of the theoretical:

0·2416 gave 0·5170 CO_2 and 0·1649 H_2O. C = 58·36; H = 7·60.
$C_{14}H_{22}O_6$ requires C = 58·7; H = 7·0 per cent.

Ethyl Carbethoxy-α*-ethylglutaconate* is a moderately viscid, colourless liquid without appreciable odour, and does not give a colour with ferric chloride. It was not thought necessary, in this case, to collect the ethyl carbonate formed in the reaction, but its presence was obvious, both from the odour and from the large quantity of material of low boiling point present.

α(or γ)*-Ethylglutaconic Acid,* $CO_2H\cdot CEt\cdot CH(H)\cdot CH\cdot CO_2H$.

In the first instance we repeated the work of Guthzeit and Dressel (*Ber.*, 1890, **23**, 3182) on the preparation of this acid from ethyl dicarbethoxy-α-ethylglutaconate in order to satisfy ourselves that the same substance was produced by both acid and alkaline hydrolysis. This we found to be the case, but the melting point

of the acid (118—120°) given by the above chemists is much too low; the acid when pure melts at 133—134°.

From Ethyl Carbethoxy-α-ethylglutaconate: Acid Hydrolysis.—The method was the same as that employed in the preparation of α-methylglutaconic acid. The crude acid melted at 128—131°, and when recrystallised from water melted at 133—134°. Some ethylmalonic acid (m. p. 112°) was found in the mother liquor from this hydrolysis. (Found, C = 45·2; H = 6·08. Calc., C = 45·5; H = 6·1 per cent.)

Alkaline Hydrolysis.—The process was the same as with α-methylglutaconic acid, and the sodium salt, $CO_2Na\cdot CEt\colon CH\cdot CNa(CO_2Na)_2$, was obtained. The salt when dissolved in water and acidified with hydrochloric acid yielded on extraction with ether an acid melting at 128—130°, which after recrystallisation from water melted at 133—134°:

0·2294 gave 0·4476 CO_2 and 0·1294 H_2O. C = 53·22; H = 6·27.
$C_7H_{10}O_4$ requires C = 53·2; H = 6·3 per cent.

This form of α-ethylglutaconic acid evidently represents the *trans*-modification corresponding with *trans*-α-methylglutaconic acid melting at 145—146°. An acid of lower melting point which is prepared by the action of potassium hydroxide on the chloroanhydride of the acid will be described in Part II. of this series.

Ethyl αγ-Dicarbethoxy-α-benzylglutaconate,
$(CO_2Et)_2C(CH_2Ph)\cdot CH\colon C(CO_2Et)_2$.

The preparation of this substance was carried out in the same manner as that employed for the production of the alkyl derivatives already described. The oil boiled at 253°/18 mm., and set to a solid mass on cooling. The melting point of this ester (78°) showed it to be the same substance as prepared by Ruhemann (Trans., 1893, **63**, 259) and by Conrad and Guthzeit (*Annalen*, 1883, **222**, 261).

Ethyl γ-Carbethoxy-α-benzylglutaconate,
$CO_2Et\cdot C(CH_2Ph)\cdot CH(H)\cdot C(CO_2Et)_2$.

Thirty-five grams of ethyl dicarbethoxy-α-benzylglutaconate were dissolved in an equal volume of alcohol and mixed with a solution containing 1·9 grams of sodium dissolved in 25 c.c. of alcohol. The solution, which became deep orange and slightly warm, was kept at the ordinary temperature for twelve hours, when it was poured into dilute hydrochloric acid and the oil extracted by ether. The ethereal extract was then purified in the usual manner, and the oil which remained on evaporation distilled under diminished pressure. Ethyl carbonate, recognisable by its odour, passed over

first, but was not collected; the triethyl ester then distilled as a colourless, fairly viscid liquid at 218°/22 mm.:

0·2292 gave 0·5494 CO_2 and 0·1448 H_2O. C = 65·37; H = 7·02.

$C_{19}H_{24}O_6$ requires C = 65·5; H = 6·9 per cent.

An alcoholic solution of ethyl carbethoxy-α-benzylglutaconate gives a reddish-brown colour with ferric chloride.

Ethyl 6-*Ethoxy*-3-*benzyl*-α-*pyrone*-5-*carboxylate*,

$$\begin{array}{l} CH_2Ph\cdot\underset{|}{C}\colon CH\cdot C(CO_2Et)\colon\underset{|}{C}\cdot OEt \\ \quad\quad\quad\; CO\text{———————}O \end{array}.$$

—There is always a quantity of material of higher boiling point formed in this reaction, and its presence is evidently caused by the decomposition of ethyl carbethoxy-α-benzylglutaconate during distillation, as when the pure triethyl ester is again distilled a further quantity of the fraction of higher boiling point is obtained. The pure decomposition product boils at 261°/25 mm., and sets to a crystalline mass on cooling. It crystallises from dilute alcohol in voluminous needles melting at 70°:

0·2044 gave 0·5044 CO_2 and 0·1095 H_2O. C = 67·35; H = 5·97.

$C_{17}H_{18}O_5$ requires C = 67·6; H = 6·0 per cent.

The ester yields α-benzylglutaconate acid on alkaline hydrolysis.

α(or γ)-*Benzylglutaconic Acid*, $CO_2H\cdot C(CH_2Ph)\cdot CH(H)\cdot CH\cdot CO_2H$.

This acid is the sole product formed by the hydrolysis of ethyl dicarbethoxy-α-benzylglutaconate by either hydrochloric acid or alcoholic potassium hydroxide. It crystallises from water in clusters of needles melting at 153—154°. (Found, C = 65·40; H = 5·60. Calc., C = 65·5; H = 5·5 per cent.) In order to show the identity of the α- and γ-positions, the same process was adopted as with the α-methyl and α-ethyl acids. In this case, however, the quantity of sodium salt precipitated by the action of alcoholic sodium ethoxide containing a little water was much smaller than would be caused by the conversion of the ester into the sodium salt. When this salt was dissolved in water and acidified, a soluble acid was extracted by ether, which when recrystallised from an equal volume of concentrated hydrochloric acid and water melted at 120°, and was proved to be benzylmalonic acid. (Found, C = 61·67; H = 5·06. Calc., C = 61·9; H = 5·2 per cent. *Silver salt:* Found, Ag = 53·0. Calc., Ag = 53·0 per cent.)

The filtrate from the sodium salt yielded benzylglutaconic acid melting at 153—154°. This acid is probably the *trans*-modification of α-benzylglutaconate acid, as there is an acid of lower melting point which can be prepared from the chloro-anhydride by the action of potassium hydroxide. This substance, which is evidently

the *cis*-modification, crystallises from water in small plates, melting at 139°.

A full description of the preparation and properties of these substances will be found in Part II.

Ethyl Carbethoxy-αγ-dimethylglutaconate,

$CO_2Et{\cdot}CMe{:}CH{\cdot}CMe(CO_2Et)_2$.

This substance was usually prepared by treating the alcoholic solution of the sodium compound formed as described on p. 2197 with 20 per cent. excess of methyl iodide, and warming on the water-bath until the yellow colour of the solution was discharged. The product was then poured into water, and the oil extracted by ether. It was soon evident that the large quantity of methyl iodide used in the experiment had caused a partial conversion of the triethyl ester, and it was found possible by working with large quantities and isolating the first and last runnings from the distillation to obtain the triethyl and methyl diethyl esters in a condition sufficiently pure for analysis. It is, of course, well known that interchange of alkyloxy-groups frequently occurs in reactions of this type, but as it was necessary for our purpose to establish the constitution of our product, we thought it desirable, in one instance, to isolate the two esters and to hydrolyse them separately. With this object in view, 109 grams of ethyl dicarbethoxy-α-methylglutaconate were mixed with 60 c.c. of alcohol, and treated with a solution containing 7·3 grams of sodium dissolved in 90 c.c. of alcohol. After an hour 55 grams of methyl iodide were added, and the solution was heated on the water-bath until the yellow colour had disappeared. Water was then added, and the ethyl ester isolated in the usual way.

Methyl Diethyl Carbethoxy-αγ-dimethylglutaconate.—As soon as all ethyl carbonate had distilled over, the temperature remained constant at 175°/20 mm., and the small fraction collected at this temperature was analysed:

0·2243 gave 0·4719 CO_2 and 0·1519 H_2O. C=57·42; H=7·51.

$C_{13}H_{20}O_6$ requires C=57·4; H=7·4 per cent.

Ethyl Carbethoxy-αγ-dimethylglutaconate.—The temperature then rose slowly, while the greater portion of the ester distilled over. It finally remained constant at 178°/20 mm., and the small fraction distilling at this temperature was analysed:

0·2397 gave 0·5167 CO_2 and 0·1656 H_2O. C=58·78; H=7·67.

$C_{14}H_{22}O_6$ requires C=58·7; H=7·7 per cent.

The two esters were hydrolysed separately by means of dilute hydrochloric acid, and as in each case αγ-dimethylglutaconic acid

was obtained as sole product, it is evident that they have the structures assigned to them above.

In the other cases of this kind which occur in this paper it was not thought necessary to isolate the two ethyl esters, and the last constant fraction was always analysed, unless stated otherwise.

Ethyl αγ-Dimethylglutaconate, $CO_2Et\cdot CMe\cdot CH(H)\cdot CMe\cdot CO_2Et$.

The conversion of ethyl carbethoxy-αγ-dimethylglutaconate into ethyl carbonate and the above ester was effected in the following way: Sixty-one grams of the triethyl ester were mixed with 40 c.c. of alcohol, and treated with a cold solution of 4·9 grams of sodium in 60 c.c. of alcohol. The mixture turned yellow after a few seconds, and then became slightly warm; it was kept at the ordinary temperature for one and a-quarter hours, when it was poured into water and extracted by ether without acidifying. The oil obtained on evaporating the dried ethereal solution was distilled under the ordinary pressure until the thermometer registered 135°, when the oil remaining was distilled under diminished pressure. The whole amount distilled between 174—176°/81 mm., and the last runnings, constituting the above ester, were analysed:

0·2265 gave 0·4979 CO_2 and 0·1647 H_2O. C = 59·95; H = 8·10.

$C_{10}H_{16}O_4$ requires C = 60·0; H = 8·0 per cent.

The large fraction obtained by distilling under ordinary pressure as described above was again distilled, and the fraction boiling at 126° was shown to be ethyl carbonate. (Found, C = 50·70; H = 8·36. Calc., C = 50·9; H = 8·5 per cent.)

The above conversion under the experimental conditions described was practically quantitative. When it is desired to prepare αγ-dimethylglutaconic acid in quantity, it is always advisable to hydrolyse the dialkyl rather than the triethyl ester. It was found that the tertiary esters of the type

$$CO_2R\cdot CMe\colon CH\cdot CMe(CO_2R)_2,$$

are only very slowly hydrolysed by dilute hydrochloric acid, whereas the "mobile" ethyl esters, $CO_2R\cdot CMe\cdot CH(H)\cdot CMe\cdot CO_2R$, are rapidly converted into the acid under the same conditions.

αγ-Dimethylglutaconic Acid, $CO_2H\cdot CMe\cdot CH(H)\cdot CMe\cdot CO_2H$.

This acid is obtained in a yield of 90 per cent. of the theory when the dialkyl ester is boiled with ten times its volume of 10 per cent. hydrochloric acid until all oil has passed into solution. The greater proportion of the acid separates when the clear hydrochloric acid solution is cooled, and a further quantity is obtained on evaporating the filtrate to a small bulk.

Forty grams of the dialkyl ester gave in this way 23 grams of acid melting at 145—147°, which separated directly from the hydrochloric acid solution; a further 3 grams, melting at 137—142°, were obtained on evaporating the filtrate. Both products when recrystallised once from dilute hydrochloric acid gave pure $\alpha\gamma$-dimethylglutaconic acid, melting at 147°. (Found, C = 53·20; H = 6·28. Calc., C = 53·2; H = 6·3 per cent.)

The constitution of this acid was proved, both by the formation of methylmalonic acid from it on oxidation with alkaline permanganate and by direct comparison with a specimen of $\alpha\gamma$-dimethylglutaconic acid prepared by Reformatzky's method from ethyl β-hydroxy-$\alpha\gamma$-dimethylglutarate,

$$CO_2H{\cdot}CHMe{\cdot}CH(OH){\cdot}CHMe{\cdot}CO_2H,$$

which was kindly sent us by Professor Feist.

The *silver* salt is a curdy, white precipitate:

0·4055 gave 0·2338 Ag. Ag = 57·74.

$C_7H_8O_4Ag_2$ requires Ag = 58·0 per cent.

Ethyl Carbethoxy-γ-methyl-α-ethylglutaconate, $CO_2Et{\cdot}CMe{:}CH{\cdot}CEt(CO_2Et)_2$.

This ester may be prepared by treating the sodium derivative obtained by the action of sodium ethoxide on ethyl dicarbethoxy-α-methylglutaconate as described on p. 2197 with ethyl iodide. Forty grams of ethyl dicarboxy-α-methylglutaconate were mixed with 30 grams of alcohol, and a solution containing 3 grams of sodium dissolved in 40 c.c. of alcohol were added. After the mixture had been kept at the ordinary temperature for one hour, 30 grams of ethyl iodide were added, and the solution was heated on the water-bath for twelve hours. The pale yellow solution was then poured into water, and the ester isolated in the usual way. The oil when fractionated yielded the usual amount of ethyl carbonate and a constant fraction boiling at 180°/20 mm. Yield, 80 per cent. of the theoretical:

0·2018 gave 0·4427 CO_2 and 0·1487 H_2O. C = 59·83; H = 8·19.

$C_{15}H_{24}O_6$ requires C = 60·0; H = 8·0 per cent.

The fractionation has, however, to be carefully conducted, because a small quantity of the diethyl ester is also formed in the reaction. This secondary change is evidently due to the partial dissociation of the sodium compound in solution.

Ethyl α-Methyl-γ-ethylglutaconate,
$CO_2Et\cdot CMe\cdot CH(H)\cdot CEt\cdot CO_2Et_2$.

The transformation of ethyl carbethoxy-γ-methyl-α-ethylglutaconate into ethyl carbonate and the above ester was effected in the usual manner: Twenty grams of the ester were dissolved in 10 c.c. of alcohol, and mixed with a solution containing 1·6 grams of sodium dissolved in 20 c.c. of alcohol. The solution, which slowly became yellow and developed a slight amount of heat, was kept at the ordinary temperature for two hours, and then worked up as usual. The oil obtained distilled at 163°/23 mm.:

0·2177 gave 0·5027 CO_2 and 0·1746 H_2O. C = 62·96; H = 8·91.
$C_{12}H_{20}O_4$ requires C = 63·1; H = 8·8 per cent.

The yield of the diethyl ester by this process is almost quantitative. The ethyl carbonate formed in the reaction was refractionated under ordinary pressure, and the large fraction boiling at 126° was collected. (Found, C = 50·71; H = 8·59. Calc., C = 50·8; H = 8·5 per cent.)

Ethyl Carbethoxy-α-methyl-γ-ethylglutaconate,
$CO_2Et\cdot CEt{:}CH\cdot CMe(CO_2Et)_2$.

The preparation of this substance from ethyl dicarbethoxy-α-ethylglutaconate (see p. 2199) was effected in the following manner: Sixty-two grams of the ester were mixed with 40 c.c. of alcohol, and a solution containing 4 grams of sodium dissolved in 50 c.c. of alcohol was added. After three hours at the ordinary temperature, 30 grams of methyl iodide were added, and the mixture heated on the water-bath for eight hours, by which time the strong yellow colour of the liquid had almost disappeared. The product was then poured into water, and the oil isolated in the usual manner. After the ethyl carbonate had been removed by distillation under ordinary pressure, the residue was fractionated under diminished pressure, and the small fraction boiling at 180°/23 mm. was collected:

0·2347 gave 0·5078 CO_2 and 0·1654 H_2O. C = 59·01; H = 7·82.
$C_{14}H_{22}O_6$ requires C = 58·7; H = 7·7 per cent.

This is therefore the methyl diethyl ester formed as explained on p. 2202. The main bulk of the product distilled between 180° and 183°, the yield of methyl diethyl and triethyl esters representing about 80 per cent. of the theoretical amount.

Ethyl α-Methyl-γ-ethylglutaconate, $CO_2Et\cdot CMe\cdot CH(H)\cdot CEt\cdot CO_2Et$.

Although we have no direct evidence that the ethyl esters prepared by the elimination of a carbethoxyl group from ethyl carbethoxy-γ-methyl-α-ethylglutaconate and ethyl carbethoxy-α-methyl-γ-ethylglutaconate respectively are the same substance, excepting that they yield the same acid on hydrolysis, yet from the identity of the corresponding acids which we have established in this communication it would be unreasonable to suppose that the ethyl esters of the acids can be different compounds. We have therefore given to the above ethyl ester the same name and formula as that assigned to the ester described on p. 2205. The diethyl ester is prepared from ethyl carbethoxy-α-methyl-γ-ethylglutaconate as follows: Thirty grams of the mixed esters prepared as described above were dissolved in 15 c.c. of alcohol, and treated with a solution containing 2·3 grams of sodium dissolved in 30 c.c. of alcohol. The mixture was kept for three hours at the ordinary temperature, when it was poured into water and extracted by ether without acidifying. After the ethereal solution had been purified in the usual manner, the residual oil was distilled free from ethyl carbonate under ordinary pressure, and the remainder fractionated under diminished pressure. A small portion which distilled first at 160°/21 mm. was analysed:

0·2111 gave 0·4782 CO_2 and 0·1573 H_2O. C=61·77; H=8·30.

$C_{11}H_{18}O_4$ requires C=61·7; H=8·4 per cent.

The liquid was therefore the methyl ethyl ester. The main bulk of the product distilled at 160—163°/21 mm., the yield of the mixed esters being practically quantitative.

The ethyl carbonate formed in the reaction was obtained by refractionating the material of low boiling point, the portion boiling at 126° being analysed. (Found, C=50·70; H=8·45. Calc., C=50·0; H=8·5 per cent.)

α-Methyl-γ-ethylglutaconic Acid, $CO_2H\cdot CMe\cdot CH(H)\cdot CEt\cdot CO_2H$.

For the sake of convenience we have placed all the experiments relating to this acid under one heading, but in order to show the identity of α-methyl-γ-ethylglutaconic acid and γ-methyl-α-ethylglutaconic acid it was necessary to prepare it by four different processes:

(1) *From Ethyl Carbethoxy-γ-methyl-α-ethylglutaconate by Alkaline Hydrolysis.*—Ten grams of the ester were added to an alcoholic solution containing 2·3 grams of sodium in 40 c.c. of alcohol, to which 5 c.c. of water had been added. A gelatinous

sodium salt slowly separated when the solution was warmed on the water-bath, and was collected. The salt was then thoroughly mixed with cold alcohol and again collected, this process being repeated three times. The salt still retained its gelatinous nature, but in spite of that was quite easy to filter; it was spread on a porous plate, and dried at 80°, when it was obtained as a fine, white powder:

0·3143 gave 0·2358 Na_2SO_4. Na = 24·31.

$C_9H_9O_6Na_3$ requires Na = 24·5 per cent.

This substance was therefore the sodium salt,

$CO_2Na\cdot CMe\dot{:}CH\cdot CEt(CO_2Na)_2$.

The Acid from the Sodium Salt.—The salt was dissolved in a little ice-cold water, and the clear solution cautiously acidified by the addition of the calculated quantity of hydrochloric acid, when a vigorous evolution of carbon dioxide ensued. The solution, which had become turbid owing to the separation of the acid as an oil, was extracted by ether, and the ethereal extract dried and evaporated. The residual gum was then dissolved in a little water, and the acid allowed to crystallise. It melted at 114—115°, and after being recrystallised from water, at 116°.

(2) *From Ethyl γ-Methyl-α-ethylglutaconate by Acid Hydrolysis.* Ten grams of the ester were mixed with ten times its volume of 10 per cent. hydrochloric acid, and heated on the sand-bath until all oil had passed into solution. The acid separated as a gum when the hydrochloric acid solution was cooled, but when the liquid was scratched with a crystal of the acid obtained in the previous experiment while still warm, the acid separated in the crystalline condition. The crude product melted at 113—115°, and, after being recrystallised from water, at 116°. The identity of this acid with that obtained in the first experiment was established by direct comparison:

0·2105 gave 0·4297 CO_2 and 0·1366 H_2O. C = 55·67; H = 7·22.

$C_8H_{12}O_4$ requires C = 55·8; H = 7·0 per cent.

(3) *From Ethyl Carbethoxy-α-methyl-γ-ethylglutaconate by Alkaline Hydrolysis.*—The conditions of this experiment were essentially the same as those described in experiment (1), and a similar salt was obtained:

0·3040 gave 0·2289 Na_2SO_4. Na = 24·39.

$C_9H_9O_6Na_3$ requires Na = 24·5 per cent.

This substance was therefore the sodium salt,

$CO_2Na\cdot CEt\dot{:}CH\dot{:}CMe(CO_2Na)_2$.

Conversion into the Acid.—The salt was dissolved in a little ice-cold water, and the clear solution cautiously acidified by the

addition of the calculated quantity of hydrochloric acid. A vigorous evolution of carbon dioxide took place, and the solution became turbid owing to the separation of the acid, which melted at 116°, after having been once recrystallised from water.

(4) *From Ethyl α-Methyl-γ-ethylglutaconate by Acid Hydrolysis.*—The same conditions as in experiment (2) were observed, and an acid melting at 116° was obtained. A direct comparison of this acid with that obtained in experiment (3) showed them to be the same substance:

0·2336 gave 0·4788 CO_2 and 0·1456 H_2O. C=55·89; H=6·94.

$C_8H_{12}O_4$ requires C=55·8; H=7·0 per cent.

The identity of the four acids obtained by the processes was established by the mixed melting-point method, and by the conversion of each product into the hydroxy-anil described below. The acid crystallises from benzene in small needles; the crystals from water are not well defined.

The Hydroxy-anil of α-Methyl-γ-ethylglutaconic Acid.—A description of the aniline derivatives of α-methyl-γ-ethylglutaconic acid will be given in a future communication, but it is necessary here to give a brief account of the preparation of this anil, as its production was used as a means of identifying the acids prepared by the methods given above. It is formed when the acid is boiled with excess of aniline for two hours, and can be isolated by pouring the product into dilute hydrochloric acid, extracting the insoluble oil by means of ether, and shaking the ethereal solution with aqueous sodium carbonate. The oil which separates when the alkaline washings are acidified slowly becomes solid, and crystallises from dilute alcohol in long needles, melting at 92°.

THE SORBY RESEARCH LABORATORY,
THE UNIVERSITY, SHEFFIELD.

CCXLVIII.—*The Chemistry of the Glutaconic Acids. Part II. The Reactions of the Alkylglutaconic Acids Having one Mobile Hydrogen Atom.*

By FERDINAND BERNARD THOLE and JOCELYN FIELD THORPE.

FOR the purposes of the present papers we have divided the acids of the glutaconic acid series into three classes, namely:

Class I.—Containing those alkyl derivatives in which there is no mobile hydrogen atom, or, in other words, those compounds in which both hydrogen atoms attached to the α-carbon atom are

replaced. A typical member of this class is $\alpha\alpha$-dimethylglutaconic acid, $CO_2H \cdot CMe_2 \cdot CH{:}CH \cdot CO_2H$.

Class II.—Containing those alkyl derivatives in which there is one mobile hydrogen atom, that is to say, those in which one hydrogen atom of the methylene group is displaced by an alkyl radicle, as in α-methylglutaconic acid, $CO_2H \cdot CHMe \cdot CH{:}CH \cdot CO_2H$, or, as we prefer to write the formula, $CO_2H \cdot CMe \cdot CH(H) \cdot CH \cdot CO_2H$.

Class III.—Containing those compounds in which both hydrogen atoms of the methylene group are free, as in glutaconic acid itself, and the β-monoalkyl derivatives, such as β-methylglutaconic acid, $CO_2H \cdot CH_2 \cdot CMe{:}CH \cdot CO_2H$ or $CO_2H \cdot CH \cdot CMe(H) \cdot CH \cdot CO_2H$.

As regards a compound falling within class I, the fixing of the double bond causes it to exhibit all the properties of a maleic or fumaric acid, and to exist in well-defined *cis-* and *trans*-modifications, which may be represented by the formulæ:

$$\begin{array}{r} CO_2H \cdot CR_2 \cdot CH \\ \| \\ CO_2H \cdot CH \end{array} \qquad\qquad \begin{array}{l} \quad\quad\;\; CH \cdot CR_2 \cdot CO_2H \\ \quad\quad\;\; \| \\ CO_2H \cdot CH \end{array}$$

cis-. *trans-*.

The known acids of this class may be summarised as follows:

	trans-.	*cis-*.	Anhydride.	Semi-anilide
$\alpha\alpha$-Dimethylglutaconic acid,* $CO_2H \cdot CMe_2 \cdot CH{:}CH \cdot CO_2H$	172°	134—135°	liquid	164°
$\alpha\alpha\beta$-Trimethylglutaconic acid,† $CO_2H \cdot CMe_2 \cdot CMe{:}CH \cdot CO_2H$	148	133	107°	138
$\alpha\alpha\gamma$-Trimethylglutaconic acid,‡ $CO_2H \cdot CMe_2 \cdot CH{:}CMe \cdot CO_2H$	150	125	88	—

* Perkin and Smith (Trans., 1903, **83**, 8); Henrich (*Monatsh.*, 1899, **20**, 560); Perkin (Trans., 1902, **81**, 253); Blaise (*Compt. rend.*, 1903, **136**, 381, 692).

† Perkin and Thorpe (Trans., 1897, **71**, 1182); Perkin and Smith (Trans., 1903, **83**, 774).

‡ Perkin and Smith (Trans., 1903, **83**, 771; 1904, **85**, 155).

So far, therefore, as the reactions of the mobile hydrogen atom are concerned, these compounds are without interest, as their reactions are in all respects normal. It is only with the members of classes II and III that the remarkable properties which we shall show are associated with the presence of the mobile hydrogen atom are in evidence; it is therefore with some of the acids of class II that we propose to deal in the present section, reserving a description of other acids for subsequent parts of this series.

It is apparent that the acids falling within class II may be of three types: (*a*) the monosubstituted derivatives, as α-methylglutaconic acid, $CO_2H \cdot CHMe \cdot CH{:}CH \cdot CO_2H$; (*b*) the disubstituted derivatives, such as $\alpha\beta$-dimethylglutaconic acid,

$$CO_2H \cdot CHMe \cdot CMe{:}CH \cdot CO_2H,$$

and $\alpha\gamma$-dimethylglutaconic acid, $CO_2H \cdot CHMe \cdot CH{:}CMe \cdot CO_2H$; and

(*c*) the trisubstituted derivatives, such as $\alpha\beta\gamma$-trimethylglutaconic acid, $CO_2H\cdot CHMe\cdot CMe\colon CMe\cdot CO_2H$. In the present paper we propose to deal with these derivatives in the above order.

(*a*) *The Monosubstituted Derivatives.*—The known acids of this type may be summarised as follows:

α-Methylglutaconic Acid, $CO_2H\cdot CHMe\cdot CH\colon CH\cdot CO_2H$.—This acid has been prepared by Conrad and Guthzeit (*Annalen*, 1883, **222**, 259), Ruhemann (Trans., 1893, **63**, 880), Smoluchowsky (*Monatsh.*, 1894, **15**, 56), and by Feist and Pomme (*Annalen*, 1909, **370**, 61). The stable form of the acid is undoubtedly the *trans*-*modification, which melts, as found by Feist and Pomme, at 145—146°. This is, moreover, the chief form in which the acid is obtained, both by the acid or alkaline hydrolysis of its esters. The last-named investigators were unable to cause the acid to react with acetyl chloride, but prepared an anhydride, melting at 85°, through the agency of phosphorus pentachloride. From this anhydride they prepared a semianilide, melting at 165°, and an unstable *cis*-acid, melting at 118°. They also prepared an anil, melting at 229°, by treating the acid of higher melting point with aniline at 150°.

α-Ethylglutaconic Acid, $CO_2H\cdot CHEt\cdot CH\colon CH\cdot CO_2H$.—This acid has been prepared by Guthzeit and Dressel (*Ber.*, 1890, **23**, 3182). The melting point is given as 118—120°, but, as we have shown in Part I. of this series, this is much too low, and the acid when pure melts at 133—134°. No other derivatives of this acid have been described.

α-Benzylglutaconic Acid, $CO_2H\cdot CH(CH_2Ph)\cdot CH\colon CH\cdot CO_2H$.—This acid has been prepared by Conrad and Guthzeit (*Annalen*, 1883, **222**, 261), Ruhemann (Trans., 1893, **63**, 259), Guthzeit and Laska (*J. pr. Chem.*, 1896, [ii], **54**, 369), and by Guthzeit and Bolam (*ibid.*, 1898, [ii], **58**, 428). We find the melting point to be 153—154°, which is a little higher than that previously recorded. No derivatives of this acid seem to have been described.

We have selected these three acids for experiment as being typical of the α-monosubstituted derivatives of glutaconic acid, and the results of our experiments are briefly as follows:

These compounds react with acetyl chloride at the temperature of the boiling reagent, but under these conditions the interaction is slow, and is rarely complete. In sealed tubes at 100°, however, the action is rapid, and after four hours no unchanged acid remains. The product is not the true anhydride, but is a mixture

* The terms *cis*- and *trans*- are used in this paper in connexion with the acids of classes II and III for the sake of convenience pending a discussion of the subject in a subsequent part of the series. For the same reason the older formulæ for the "mobile" acids are retained in the introduction to this part.

of two substances, one of which is the hydroxy-anhydride (I), the other the chloro-anhydride (II):

$$\mathrm{CH}\Big<\begin{array}{l}\mathrm{CR{-\!\!-}CO}\\ \mathrm{CH{:}C(OH)}\end{array}\Big>\mathrm{O} \qquad\qquad \mathrm{CH}\Big<\begin{array}{l}\mathrm{CR{-}CO}\\ \mathrm{CH{:}CCl}\end{array}\Big>\mathrm{O}$$

(I.) (II.)

These compounds are, of course, derivatives of α-pyrone, and are so named in the experimental portion of this section, but their close relationship to the substituted glutaconic acid renders it advisable to adopt the names hydroxy-anhydride and chloro-anhydride when referring to them in the introduction.

The proportion in which these substances are formed depends entirely on the time during which the reagent is allowed to react, and on prolonged heating at 100° the chloro-anhydride is the sole product. The mechanism of this abnormal reaction is probably thus: The first action of acetyl chloride produces the normal anhydride, but at the temperature of the reaction the mobile hydrogen atom passes outside the three-carbon system to the neighbouring carbonyl group, where it is slowly attacked by acetyl chloride, yielding the acetyl-anhydride (III). This compound is, however, rapidly converted by the hydrogen chloride formed in the reaction into the chloro-anhydride, thus:

$$\mathrm{CH}\Big<\begin{array}{l}\mathrm{CR{-}CO}\\ \mathrm{CH_2{\cdot}CO}\end{array}\Big>\mathrm{O} \longrightarrow \mathrm{CH}\Big<\begin{array}{l}\mathrm{CR{-\!\!-}CO}\\ \mathrm{CH{:}C(OH)}\end{array}\Big>\mathrm{O} \longrightarrow$$

$$\mathrm{CH}\Big<\begin{array}{l}\mathrm{CR{-\!\!-}CO}\\ \mathrm{CH{:}C(OAc)}\end{array}\Big>\mathrm{O} \longrightarrow \mathrm{CH}\Big<\begin{array}{l}\mathrm{CR{-}CO}\\ \mathrm{CH{:}CCl}\end{array}\Big>\mathrm{O}$$

(III.)

Strong support is given to this view, because in one case (that of αβ-dimethylglutaconic acid) we were able to isolate the acetyl-anhydride, and to show that it was an intermediate product in the transformation of the hydroxy-anhydride into the chloro-anhydride.

As the behaviour of the derivatives of the three acids is much the same, and is only modified by the presence of the heavier grouping, the general properties of these curious substances can be indicated by referring to the α-benzyl derivatives.

The mixture of the hydroxy-anhydride and chloro-anhydride obtained by heating α-benzylglutaconic acid with acetyl chloride, is readily separated by means of ether:

$$\mathrm{CH}\Big<\begin{array}{l}\mathrm{C(CH_2Ph){\cdot}CO}\\ \mathrm{CH{=\!=}C(OH)}\end{array}\Big>\mathrm{O} \qquad\qquad \mathrm{CH}\Big<\begin{array}{l}\mathrm{C(CH_2Ph){\cdot}CO}\\ \mathrm{CH{=\!=\!=}CCl}\end{array}\Big>\mathrm{O}$$

M. p. 90°. M. p. 74°.

The hydroxy-anhydride acts as a monobasic acid, and is characterised by giving a crystalline monopotassium salt (IV), which is very soluble in water, and the solution when acidified again yields

the hydroxy-anhydride. These changes can therefore be represented thus:

$$\mathrm{CH}\Big\langle\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{CH{=\!=}C(OH)}\end{matrix}\Big\rangle\mathrm{O} \quad \underset{\text{acid}}{\overset{\text{alkali}}{\rightleftarrows}} \quad \mathrm{CH}\Big\langle\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{CH{=\!=}C(OK)}\end{matrix}\Big\rangle\mathrm{O}$$

(IV.)

When the chloro-anhydride is treated with excess of aqueous potassium hydroxide it is ultimately converted into the sparingly soluble potassium salt of the hydroxy-pyrone, from which the hydroxy-anhydride is obtained on acidifying:

$$\mathrm{CH}\Big\langle\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{CH{=\!=\!=}CCl}\end{matrix}\Big\rangle\mathrm{O} \xrightarrow{\text{KOH}} \mathrm{CH}\Big\langle\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{CH{=\!=}C(OK)}\end{matrix}\Big\rangle\mathrm{O} \xrightarrow{\text{acids}} \mathrm{CH}\Big\langle\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{C{=\!=\!=}C(OH)}\end{matrix}\Big\rangle\mathrm{O}.$$

When the hydroxy-anhydride is warmed with excess of potassium hydroxide, it is slowly converted into the dipotassium salt of the *cis*-acid. This acid melts at 139°, and is completely transformed into the *trans*-modification of the acid * when it is boiled for a few minutes with hydrochloric acid:

$$\mathrm{CH}\Big\langle\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{CH{=\!=}C(OH)}\end{matrix}\Big\rangle\mathrm{O} \longrightarrow \begin{matrix}\mathrm{CH_2Ph\cdot C\cdot CO_2H}\\ \Vert\\ \mathrm{CH}\\ |\\ \mathrm{CH_2\cdot CO_2H}\\ \text{M. p. 139°.}\end{matrix} \longrightarrow \begin{matrix}\mathrm{CO_2H\cdot C\cdot CH_2Ph}\\ \Vert\\ \mathrm{CH}\\ |\\ \mathrm{CH_2\cdot CO_2H}\\ \text{M. p. 153—154°.}\end{matrix}$$

When the hydroxy-anhydride is boiled with alcohol it is converted into the acid ester:

$$\mathrm{CH}\Big\langle\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{CH{=\!=}C(OH)}\end{matrix}\Big\rangle\mathrm{O} + \mathrm{ROH} \longrightarrow \begin{matrix}\mathrm{CH_2Ph\cdot C\cdot CO_2Et}\\ \Vert\\ \mathrm{CH}\\ |\\ \mathrm{CH_2\cdot CO_2H}\end{matrix}$$

The hydroxy-anhydrides and the chloro-anhydrides from the α-methyl and α-ethyl acids behave in an analogous manner, but the stability of the anhydride increases with the weight of the group attached to the α-carbon atom; thus the hydroxy-anhydride from the α-methyl acid is rapidly converted into the salt of the *trans*-acid when it is dissolved in excess of sodium hydrogen carbonate solution at the ordinary temperature, and the titration of this substance has therefore to be effected very quickly, otherwise the figures obtained are too high. The hydroxy-anhydride from the α-ethyl acid is much more stable, and can be titrated without any special precautions; but it is slowly converted into the salt of the *cis*-acid in the presence of excess of sodium hydrogen carbonate solution. The stability of the *cis*-forms of these acids increases with the molecular weight of the group occupying the α-position,

* See footnote, p. 2210.

but the *cis*-form is always produced when the anhydride is hydrolysed by strong alkali hydroxide or by alkali carbonates in the presence of casein.

In the above description of the hydroxy-anhydrides and chloroanhydrides it will be noticed that we have assigned to them a constitution in which the substituting group is attached to the γ-carbon atom. It is, of course, obvious that in these substances the double bonds must be fixed, and that the virtual tautomerism of the glutaconic acid ceases when the mobile hydrogen passes outside the three-carbon system. There must, therefore, be two forms of these compounds, which can be represented in the case of the hydroxy-anhydride by the formulæ V and VI:

$$\mathrm{CH}{<}\begin{matrix}\mathrm{CR}\text{——}\mathrm{CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}{>}\mathrm{O} \quad \text{and} \quad \mathrm{CH}{<}\begin{matrix}\mathrm{CR{:}C(OH)}\\ \mathrm{CH}\text{——}\mathrm{CO}\end{matrix}{>}\mathrm{O}$$

(V.) (VI.)

We are satisfied that the compounds described by us have a structure represented by formula V, because they yield no trace of a pyruvic acid on oxidation, but give oxalic acid as chief product. It is probable that compounds constituted as in formula VI would give pyruvic acid or a homologue under these conditions.

The normal anhydrides of the α-substituted glutaconic acids are formed, as Feist and Pomme (*loc. cit.*) have shown in the case of the α-methyl acid, by treating the acid with sufficient phosphorus pentachloride to convert it into the monoacid chloride when a reaction ensues, which is represented by the equation:

$$\mathrm{CH}{<}\begin{matrix}\mathrm{CHR{\cdot}CO_2H}\\ \mathrm{CH{\cdot}COCl}\end{matrix} \longrightarrow \mathrm{CH}{<}\begin{matrix}\mathrm{CHR{\cdot}CO}\\ \mathrm{CH{-}CO}\end{matrix}{>}\mathrm{O} + \mathrm{HCl}.$$

Under these conditions, therefore, the mobile hydrogen atom remains within the three-carbon system, but we find that these normal anhydrides are without exception converted into the hydroxy-anhydrides on distillation, thus:

$$\mathrm{CH}{<}\begin{matrix}\mathrm{CHR{\cdot}CO}\\ \mathrm{CH{-}CO}\end{matrix}{>}\mathrm{O} \longrightarrow \mathrm{CH}{<}\begin{matrix}\mathrm{CR}\text{——}\mathrm{CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}{>}\mathrm{O}.$$

The Aniline Derivatives of the α-Substituted Glutaconic Acids.—Up to the present time the only derivatives of this type which have been described are a semianilide, melting at 165°, which Feist and Pomme prepared from the normal anhydride of α-methylglutaconic acid, and an anil melting at 229°, which the same chemists prepared by heating α-methylglutaconic acid with one molecule of aniline at 150°. We have tried on several occasions to prepare the anil melting at 229°, but we have always obtained a semianilide melting at 189°. We therefore sent a small quantity of α-methylglutaconic acid to Professor Feist and asked him to prepare for us some of his anil. Strangely enough, he also obtained our semianilide melting

at 189°, and it is evident, therefore, that the preparation of the anil depends on conditions which cannot be easily reproduced. During our many experiments with *α*-methylglutaconic acid we have not as yet succeeded in isolating any aniline derivative having this melting point, and the structure of this substance must therefore remain for the present unsolved. The *trans*-modifications of *α*-methyl-, *α*-ethyl-, and *α*-benzyl-glutaconic acids behave in a precisely similar manner when heated with aniline at 150°, and yield well-defined semianilides, which, since they lose carbon dioxide when heated a few degrees above their melting points, yielding anilides of monobasic acids, are probably constituted in accordance with formula VIII:

$$\begin{array}{ccc} \begin{array}{l} CO_2H{\cdot}CH{\cdot}R \\ \quad\;\; | \\ \quad\; CH \\ \quad\;\; \| \\ \quad\; CH{\cdot}CO{\cdot}NHPh \\ \qquad (VII). \end{array} & \qquad\qquad & \begin{array}{l} CO_2H{\cdot}CH_2 \\ \quad\;\; | \\ \quad\; CH \\ \quad\;\; \| \\ \;R{\cdot}C{\cdot}CO{\cdot}NHPh \\ \qquad (VIII.) \end{array} \end{array}$$

The only other formula for a semianilide losing carbon dioxide in this manner would be formula VII. That the semianilides prepared by us have a structure represented by formula VIII is proved by the formation of malonic acid from them on oxidation. It is clear that a compound of formula VII would give the alkylmalonic acid when oxidised.

The *cis*-modifications of the three *α*-substituted acids also give, on heating with aniline,* the *trans*-modifications of the semianilides identical with those prepared from the *trans*-acids, and it is evident, therefore, that a complete rearrangement to the stable *trans*-form occurs at the temperature of the reaction. The *cis*-modifications of the semianilide can, however, be readily prepared from the hydroxy-anhydrides by warming them in benzene solution with aniline, thus:

$$CH{<}\begin{array}{l} CR\text{——}CO \\ CH{:}C(OH) \end{array}{>}O \longrightarrow \begin{array}{l} R{\cdot}C{\cdot}CO{\cdot}NHPh \\ \;\; \| \\ \; CH \\ \;\; | \\ \; CH{:}C(OH)_2 \end{array} \longrightarrow \begin{array}{l} R{\cdot}C{\cdot}CO{\cdot}NHPh \\ \;\; \| \\ \; CH \\ \;\; | \\ \; CH_2{\cdot}CO_2H \end{array}$$

The structure of these substances is clear from the fact that on heating at 150° they are completely transformed into the *trans*-semianilides; thus the *α*-methyl derivative behaves as follows:

$$\begin{array}{ccc} \begin{array}{l} Me{\cdot}C{\cdot}CO{\cdot}NHPh \\ \quad \| \\ \quad CH \\ \quad | \\ \quad CH_2{\cdot}CO_2H \\ \;\; \text{M. p. } 148°. \end{array} & \xrightarrow{150°} & \begin{array}{r} NHPh{\cdot}CO{\cdot}C{\cdot}Me \\ \| \quad\;\; \\ CH \quad\;\; \\ | \quad\;\; \\ CH_2{\cdot}CO_2H \\ \text{M. p. } 189°. \end{array} \end{array}$$

* It is probable, and it is assumed, that these anilic acids represent true maleic and fumaric forms, and that in them the double bond is fixed.

The *cis*-semianilides prepared from the hydroxy-anhydrides are not the same compounds as are obtained from the normal anhydride and aniline; thus the *trans*-semianilide from α-methylglutaconic acid melts at 189°, whilst the *cis*-semianilide from the hydroxy-anhydride melts at 148°. The semianilide formed from the normal anhydride by Feist and Pomme melts at 165°. It is probable that this substance is formed in accordance with the following equation (see p. 2220):

$$CH{<}\begin{matrix}CHMe\cdot CO\\ CH{-\!-}CO\end{matrix}{>}O \longrightarrow \begin{matrix}Me\cdot CH\cdot CO\cdot NHPh\\ |\\ CH\\ \|\\ CH\cdot CO_2H\end{matrix}$$

M. p. 165°.

The normal anhydrides of these acids are, however, so difficult to prepare that we have not as yet been able to obtain enough of this semianilide to enable us to study the products formed from it on oxidation.

The derivatives of the α-monosubstituted glutaconic acids may therefore be summarised as follows:

	trans-Form.	*cis*-Form.	Normal anhydride.	Hydroxy-anhydride.	Chloro-anhydride.	*cis*-Semianilide.	*trans*-Semianilide	Semianilide from normal anhydride.
α-Methylglutaconic acid, $CO_2H\cdot CMe\cdot CH(\mathbf{H})\cdot CH\cdot CO_2H$ ...	145—146°	118°	85°	74·5°	71°	148°	189°	165°
α-Ethylglutaconic acid, $CO_2H\cdot CEt\cdot CH(\mathbf{H})\cdot CH\cdot CO_2H$ ...	133—134	108	liquid	liquid B.p. 175°/23.	39	121	170	149
α-Benzylglutaconic acid, $CO_2H\cdot C(CH_2Ph)\cdot CH(\mathbf{H})\cdot CH\cdot CO_2H$	153—154	139	—	90·0	74	143	175	—

The conclusion to be drawn from these experiments is that the stable form of the α-substituted acid and its derivatives at low temperatures contains the mobile hydrogen atom in the three-carbon system, but that at high temperatures the hydrogen atom passes to the carbonyl oxygen.

(*b*) *The Disubstituted Derivatives.*—There are four acids of this type known:

αβ-Dimethylglutaconic acid, $CO_2H\cdot CMe\cdot CMe(H)\cdot CH\cdot CO_2H$, has been prepared by Rogerson and Thorpe (Trans., 1905, **87**, 1696) and by Feist and Beyer (*Annalen*, 1906, **345**, 117). The acid melts at 148°, and gives a liquid anhydride boiling at 163°/15 mm.*; the semianilide prepared from this anhydride melts at 139°.

αγ-Dimethylglutaconic acid, $CO_2H\cdot CMe\cdot CH(H)\cdot CMe\cdot CO_2H$, was

* Through a clerical error the pressure given in the original paper was 25 mm.

first prepared by Reformatzky (*J. Russ. Phys. Chem. Soc.*, 1898, **30**, 453), and subsequently by Blaise (*Bull. Soc. chim.*, 1903, [iii], **29**, 1016; *Compt. rend.*, 1903, **136**, 381, 692, 1140). It has been more recently investigated by Feist and Reuter (*Annalen*, 1909, **370**, 82), but these chemists were unable to cause the acid to react with acetyl chloride.

β-Methyl-α-ethylglutaconic acid, $CO_2H{\cdot}CEt{\cdot}CMe(H){\cdot}CH{\cdot}CO_2H$, has been prepared by Rogerson and Thorpe (Trans., 1905, **87**, 1709). It melts at 164°, gives an anhydride melting at 53°, and a semianilide melting at 129°.

α-Methyl-γ-ethylglutaconic acid, $CO_2H{\cdot}CMe{\cdot}CH(H){\cdot}CEt{\cdot}CO_2H$, is described in Part I. of this series (this vol., p. 2197).

Of these acids we propose here to describe only the *αβ*- and *αγ*-dimethyl derivatives, leaving the other acids of this series to be dealt with in a subsequent paper.

It is certainly remarkable that Feist and Reuter should have been unable to cause the *αγ*-dimethyl acid to react with acetyl chloride, because in our hands interaction between these substances proceeded smoothly and rapidly at the temperature of the boiling reagent. The probable cause of this discrepancy has revealed itself during some recent experiments with glutaconic acid. This acid does not react with Kahlbaum's pure acetyl chloride under the conditions given by Buchner (*Ber.*, 1894, **27**, 382), but readily does so with Kahlbaum's "Acetyl chloride II." The presence of traces of phosphorus trichloride or phosphoryl chloride in the less pure reagent presumably acts as a "catalyst."

αβ-Dimethylglutaconic Acid.—This acid is converted into the anhydride when it is heated a few degrees above its melting point. The anhydride is also formed when the acid is heated for from ten to fifteen minutes on the water-bath with acetyl chloride, but under these conditions the product consists for the most part of the hydroxy-anhydride, and is composed entirely of this substance if the heating with acetyl chloride is continued for one hour. As, moreover, the normal anhydride is completely converted into the hydroxy-anhydride on distillation, it is evident that the compound described in the former paper as the normal anhydride must be the hydroxy-anhydride of formula IX. This conclusion was tested by a titration of the anhydride, when figures corresponding with the formation of the salt of the hydroxy-pyrone (X) were obtained:

$$\underset{\text{(IX.)}}{CMe{<}\begin{matrix}CMe{-}{-}CO\\CH{:}C(OH)\end{matrix}{>}O} \quad \underset{\text{alkali}}{\overset{\text{acids}}{\begin{matrix}\leftarrow\\\rightarrow\end{matrix}}} \quad \underset{\text{(X.)}}{CMe{<}\begin{matrix}CMe{-}{-}CO\\CH{:}C(ONa)\end{matrix}{>}O}$$

When the cold neutral solution of the salt is acidified, the hydroxy-anhydride is again precipitated, and at the ordinary

temperature there appears to be little tendency for the mobile hydrogen atom to re-enter the three-carbon system; but this change takes place with great rapidity when the solution is boiled, yielding the sodium hydrogen salt of the original acid *:

$$\mathrm{CMe}{<}\begin{array}{l}\mathrm{CMe}\text{——}\mathrm{CO}\\ \mathrm{CH{:}C(ONa)}\end{array}{>}\mathrm{O} + \mathrm{H_2O} \longrightarrow \mathrm{CMe}{<}\begin{array}{l}\mathrm{CMe{\cdot}CO_2H}\\ \mathrm{CH_2{\cdot}CO_2Na}\end{array} \longrightarrow$$

$$\mathrm{CMe}{<}\begin{array}{l}\mathrm{CMe{\cdot}CO_2H}\\ \mathrm{CH_2{\cdot}CO_2H}\end{array}$$

M.p. 148°.

If, therefore, the $\alpha\beta$-dimethyl acid is heated for one hour with acetyl chloride, the product after removing the reagent can be extracted entirely from its solution in ether by aqueous sodium hydrogen carbonate. After heating for six hours a considerable quantity of solid remains dissolved in the ether, and this was proved to be the acetyl-anhydride (XI). No trace of the chloro-anhydride is formed under these conditions:

$$\mathrm{CMe}{<}\begin{array}{l}\mathrm{CMe}\text{——}\mathrm{CO}\\ \mathrm{CH{:}C(OH)}\end{array}{>}\mathrm{O} \longrightarrow \mathrm{CMe}{<}\begin{array}{l}\mathrm{CMe}\text{——}\mathrm{CO}\\ \mathrm{CH{:}C(OAc)}\end{array}{>}\mathrm{O} \longrightarrow$$

M.p. 65°.
(XI.)

$$\mathrm{CMe}{<}\begin{array}{l}\mathrm{CMe{\cdot}CO}\\ \mathrm{CH{:}CCl}\end{array}{>}\mathrm{O}.$$

The acetyl-anhydride is readily hydrolysed to the acid from which it was derived, and its formation clearly indicates the mechanism of the reactions by which the chloro-anhydrides are produced. The chloro-anhydride of the $\alpha\beta$-dimethyl acid is difficult to prepare, but is obtained in small amount by the prolonged action of acetyl chloride at 100°, and is, moreover, formed when the acetyl anhydride is heated in a sealed tube with a solution of hydrogen chloride in acetic acid. Apart from other considerations the constitution of the acetyl-anhydride is shown by the formation of acetanilide and the semianilide of $\alpha\beta$-dimethylglutaconic acid when it is treated with excess of aniline:

$$\mathrm{CMe}{<}\begin{array}{l}\mathrm{CMe}\text{——}\mathrm{CO}\\ \mathrm{CH{:}C(OAc)}\end{array}{>}\mathrm{O} + 2\mathrm{NH_2Ph} \longrightarrow$$

$$\mathrm{CMe}{<}\begin{array}{l}\mathrm{CMe{\cdot}CO_2H}\\ \mathrm{CH_2{\cdot}CO{\cdot}NHPh}\end{array} + \mathrm{NHAcPh}.$$

$\alpha\gamma$-Dimethylglutaconic Acid.—This acid readily yields the normal anhydride, and it is therefore evident that the presence of a second methyl group attached to the γ-carbon atom has a marked restraining effect on the tendency of the mobile hydrogen atom to remain outside the three-carbon system. The normal

* Incidentally these reactions are clearly another proof of the identity of the α- and γ-positions.

anhydride can be quantitatively converted into the crystalline hydroxy-anhydride by heating:

$$\mathrm{CH}\Big<\begin{matrix}\mathrm{CHMe{\cdot}CO}\\ \mathrm{CMe{-}CO}\end{matrix}\Big>\mathrm{O} \longrightarrow \underset{\text{M.p. }74^\circ.}{\mathrm{CH}\Big<\begin{matrix}\mathrm{CMe{:}C(OH)}\\ \mathrm{CMe{-\!-\!-}CO}\end{matrix}\Big>\mathrm{O}} \longrightarrow \underset{\text{M.p. }82\text{—}83^\circ.}{\mathrm{CH}\Big<\begin{matrix}\mathrm{CMe{:}CCl}\\ \mathrm{CMe{-}CO}\end{matrix}\Big>\mathrm{O}}$$

The hydroxy-anhydride is readily produced when the acid is heated with acetyl chloride at 100°, and at the same time there is formed a small quantity of the chloro-anhydride, melting at 82—83°, which is undoubtedly the same substance as that prepared in small quantity by Feist and Reuter (*Annalen*, 1909, **370**, 84) by the action of phosphorus pentachloride on the acid. The formation of the acetyl-anhydride could not be detected, and it is evident that the acetylation, and therefore chlorination, of the hydroxy-anhydride takes place with great difficulty.

The hydroxy-anhydride on titration gives figures closely approximating to those required for the monobasic hydroxy-pyrone, but even at the ordinary temperature the passage of the mobile hydrogen atom into the three-carbon system is very rapid, and the change is complete in the course of a few minutes:

$$\mathrm{CH}\Big<\begin{matrix}\mathrm{CMe{:}C(OH)}\\ \mathrm{CMe{-\!-\!-}CO}\end{matrix}\Big>\mathrm{O} \longrightarrow \mathrm{CH}\Big<\begin{matrix}\mathrm{CMe{:}C(OK)}\\ \mathrm{CMe{-\!-\!-}CO}\end{matrix}\Big>\mathrm{O} \longrightarrow \begin{matrix}\mathrm{Me{\cdot}CH{\cdot}CO_2H}\\ |\\ \mathrm{CH}\\ \|\\ \mathrm{Me{\cdot}C{\cdot}CO_2K(H)}\end{matrix}$$

The acid produced is again the only known form of the acid.

The Aniline Derivatives of the Members of Section (*b*).—The fact that the stable form of the acids of this class form anhydrides with greater ease than the mono-α-substituted derivatives, enables them to form certain interesting derivatives with aniline, a study of which throws considerable light on the properties conferred on these compounds by the presence of the mobile hydrogen atom; for example, the hydroxy-anhydride of $\alpha\beta$-dimethylglutaconic acid yields a semianilide melting at 139°:

$$\mathrm{CMe}\Big<\begin{matrix}\mathrm{CMe{-\!-\!-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}\Big>\mathrm{O} \longrightarrow \underset{\text{M. p. }139^\circ.}{\begin{matrix}\mathrm{Me{\cdot}C{\cdot}CO_2H}\\ \|\\ \mathrm{Me{\cdot}C}\\ |\\ \mathrm{CH_2{\cdot}CO{\cdot}NHPh}\end{matrix}}$$

which gives an hydroxy-anil in accordance with the scheme:

$$\underset{\substack{\text{Semianilide,}\\ \text{m. p. }139^\circ.}}{\begin{matrix}\mathrm{Me{\cdot}C{\cdot}CO_2H}\\ \|\\ \mathrm{Me{\cdot}C}\\ |\\ \mathrm{CH_2{\cdot}CO{\cdot}NHPh}\end{matrix}} \longrightarrow \underset{\substack{\text{Hydroxy-anil,}\\ \text{m. p. }125^\circ.}}{\mathrm{CMe}\Big<\begin{matrix}\mathrm{CMe{-\!-\!-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}\Big>\mathrm{NPh}}$$

The hydroxy-anil behaves in the same manner as the hydroxy-anhydrides, and titrates as a monobasic acid. The neutral solution regenerates the hydroxy-anil when acidified, and it is therefore evident that the change must be represented by the scheme:

$$\mathrm{CMe}\Big\langle\begin{matrix}\mathrm{CMe{-\!\!-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}\Big\rangle\mathrm{NPh} \quad \underset{\text{acids}}{\overset{\text{alkali}}{\rightleftarrows}} \quad \mathrm{CMe}\Big\langle\begin{matrix}\mathrm{CMe{-\!\!-}CO}\\ \mathrm{CH{:}C(OK)}\end{matrix}\Big\rangle\mathrm{NPh.}$$

We have not yet succeeded in finding the conditions under which this substance is converted into the semianilide or normal anil, that is to say, the conditions which cause the mobile hydrogen atom to pass into the three-carbon system, and it is therefore evident that with the $\alpha\beta$-disubstituted derivatives the tendency for the mobile hydrogen atom to remain outside the three-carbon system is very considerable. Further experiments on the $\alpha\beta$-dimethyl acid and on higher members of the series are in progress, but so far we have not been able to prepare the normal anhydride of any of these acids in a pure condition.

With the $\alpha\gamma$-disubstituted derivatives the attachment of an alkyl group to the γ-carbon atom so far modifies the mobility of the hydrogen atom as to cause both forms to be stable. This decreased mobility, which is indicated by the ready manner in which both the normal and hydroxy-anhydrides can be isolated from $\alpha\gamma$-dimethylglutaconic acid, causes this acid, in the form of its aniline derivatives, to exhibit properties which may be regarded as typical of a compound belonging to this class, in which a state of equilibrium within the molecule enables either the one form or the other to be capable of isolation, and to be readily convertible the one into the other; thus, when the normal anhydride of $\alpha\gamma$-dimethylglutaconic acid is treated with aniline, a semianilide is formed, which when heated at 150° passes with loss of water into the hydroxy-anil:

$$\mathrm{CH}\Big\langle\begin{matrix}\mathrm{CMe{-\!\!-}CO}\\ \mathrm{CHMe{\cdot}CO}\end{matrix}\Big\rangle\mathrm{O} \quad \longrightarrow \quad \underset{\text{M. p. 165—166°.}}{\mathrm{CH}\Big\langle\begin{matrix}\mathrm{CMe{\cdot}CO_2H}\\ \mathrm{CHMe{\cdot}CO{\cdot}NHPh}\end{matrix}} \quad \longrightarrow$$

$$\underset{\text{M. p. 112°.}}{\mathrm{CH}\Big\langle\begin{matrix}\mathrm{CMe{-\!\!-}CO}\\ \mathrm{CMe{:}C(OH)}\end{matrix}\Big\rangle\mathrm{NPh}}$$

This hydroxy-anil behaves as a monobasic acid, and if the cold neutral solution of the salt is acidified, the unaltered anil is precipitated. If, however, the neutral solution is raised to the boiling point and then acidified, the semianilide (m. p. 166°) is obtained as sole product, showing that at 100° the re-entry of the mobile hydrogen atom into the three-carbon system with fission of

the ring is complete. This change may therefore be represented as follows:

$$\mathrm{CH}<\begin{matrix}\mathrm{CMe}\text{——}\mathrm{CO}\\ \mathrm{CMe{:}C(OH)}\end{matrix}>\mathrm{NPh}\ \underset{\text{acids}}{\overset{\text{alkali}}{\rightleftarrows}}\ \mathrm{CH}<\begin{matrix}\mathrm{CMe{\cdot}CO_2K}\\ \mathrm{CMe{:}C(OH){\cdot}NHPh}\end{matrix}$$

$$\xrightarrow{100^{\circ}}\mathrm{CH}<\begin{matrix}\mathrm{CMe{\cdot}CO_2K(H)}\\ \mathrm{CHMe{\cdot}CO{\cdot}NHPh.}\end{matrix}$$

The increased stability of the "normal" forms of these compounds causes them, moreover, to exhibit a further interesting change; thus, when a solution of the hydroxy-anil in excess of alkali is titrated with hydrochloric acid, using phenolphthalein as indicator, a definite end-point is reached corresponding with the formation of the alkali salt of the hydroxy-pyrone. On remaining for a few moments the colour of the indicator returns, showing that the solution has become again alkaline. More acid may then be added, when the colour again returns on keeping, and this process may be repeated until finally the solution remains neutral. At this stage a considerable quantity of crystalline material separates; this substance is the true anil of the acid. The filtrate from the crystalline anil yields the hydroxy-anil when acidified, and from this recovered substance more of the anil may be prepared by repeating the above process.

It is probable that this behaviour is due to the dissociation of the alkali salt in neutral solution, and the consequent migration of the mobile hydrogen atom, thus:

$$\mathrm{CH}<\begin{matrix}\mathrm{CMe}\text{——}\mathrm{CO}\\ \mathrm{CMe{:}C(OK)}\end{matrix}>\mathrm{NPh}\longrightarrow\mathrm{CH}<\begin{matrix}\mathrm{CMe}\text{——}\mathrm{CO}\\ \mathrm{CMe{:}C(OH)}\end{matrix}>\mathrm{NPh}\longrightarrow$$

$$\mathrm{CH}<\begin{matrix}\mathrm{CMe}\text{——}\mathrm{CO}\\ \mathrm{CHMe{\cdot}CO}\end{matrix}>\mathrm{NPh.}$$

There is one point respecting the semianilides of the substituted glutaconic acid which requires a brief explanation. It will be remembered that the semianilide prepared by Feist and Pomme from the normal anhydride of α-methylglutaconic acid melts at 165°, and is not the same compound as that prepared by us from the hydroxy-anhydride and aniline, which melts at 148°, and is converted on heating into the *trans*-semianilide, melting at 189°.

On the other hand, the semianilides prepared from the normal anhydride and the hydroxy-anhydride of $\alpha\gamma$-dimethylglutaconic acid and aniline are, as already mentioned, identical. The explanation of this apparent discrepancy is, however, obvious, because it is evident that, whereas there are two possible forms of the hydroxy-anhydride of α-methylglutaconic acid, namely:

$$\mathrm{CH}<\begin{matrix}\mathrm{CMe{:}C(OH)}\\ \mathrm{CH}\text{——}\mathrm{CO}\end{matrix}>\mathrm{O}\qquad\text{and}\qquad\mathrm{CH}<\begin{matrix}\mathrm{CH{:}C(OH)}\\ \mathrm{CMe}\text{——}\mathrm{CO}\end{matrix}>\mathrm{O}$$

there is only one possible modification of the hydroxy-anhydride of $\alpha\gamma$-dimethylglutaconic acid, as also of the hydroxy-anil:

$$\mathrm{CH}\left<\begin{matrix}\mathrm{CMe{:}C(OH)}\\ \mathrm{CMe{-}{-}{-}CO}\end{matrix}\right>\mathrm{O} \quad \text{and} \quad \mathrm{CH}\left<\begin{matrix}\mathrm{CMe{:}C(OH)}\\ \mathrm{CMe{-}{-}{-}CO}\end{matrix}\right>\mathrm{NPh}.$$

The semianilide which is formed from this hydroxy-anil must therefore have the structure:

$$\underset{\text{Hydroxy-anil.}}{\mathrm{CH}\left<\begin{matrix}\mathrm{CMe{:}C(OH)}\\ \mathrm{CMe{-}{-}{-}CO}\end{matrix}\right>\mathrm{NPh}} \longrightarrow \underset{\text{Semianilide.}}{\mathrm{CH}\left<\begin{matrix}\mathrm{CHMe{\cdot}CO{\cdot}NHPh}\\ \mathrm{CMe{\cdot}CO_2H}\end{matrix}\right.}$$

This, it will be noticed, is the same formula as that which we have assigned to the semianilide prepared by Feist and Pomme (see p. 2215), and it is evident, therefore, that the normal anhydrides behave in the same manner in both cases.

The derivatives of the acids of section (*b*) may be therefore summarised as follows:

	Acid.	Normal anhydride.	Hydroxy anhydride.	Chloro-anhydride.	Hydroxy-anil.	Semianilide.	Anil.
$\alpha\beta$-Dimethylglutaconic acid $CO_2H{\cdot}CMe{\cdot}CMe(H){\cdot}CH{\cdot}CO_2H$	148°	—	B. p. 183°/ 25 mm.	liquid B.p. 133°/ 26 mm.	125°	139°	—
$\alpha\gamma$-Dimethylglutaconic acid $CO_2H{\cdot}CMe{\cdot}CH(H){\cdot}CMe{\cdot}CO_2H$	147	liquid	75	82—83	112	166	174

The Acids of Section (*c*).—The only acid of this kind which is at present known is $\alpha\beta\gamma$-trimethylglutaconic acid,

$$\mathrm{CO_2H{\cdot}CMe{\cdot}CMe(H){\cdot}CMe{\cdot}CO_2H},$$

which was prepared by Rogerson and Thorpe (Trans., 1905, **87**, 1704). The acid melts at 127°, and gives an anhydride when boiled with acetic anhydride, which melts at 119°. As in the case of the $\alpha\beta$-dimethyl acid, there is no doubt that this anhydride is the hydroxy-anhydride. The normal anhydride is a liquid, and is formed by the action of boiling acetyl chloride on the acid. The normal anhydride is quite insoluble in aqueous sodium hydrogen carbonate, and when distilled is completely converted into the hydroxy-anhydride:

$$\mathrm{CMe}\left<\begin{matrix}\mathrm{CHMe{\cdot}CO_2H}\\ \mathrm{CMe{\cdot}CO_2H}\end{matrix}\right. \xrightarrow{\text{acetyl chloride}} \underset{\text{Liquid.}}{\mathrm{CMe}\left<\begin{matrix}\mathrm{CHMe{\cdot}CO}\\ \mathrm{CMe{-}CO}\end{matrix}\right>\mathrm{O}} \xrightarrow{\text{distillation}}$$

$$\underset{\text{M. p. 119°.}}{\mathrm{CMe}\left<\begin{matrix}\mathrm{CMe{:}C(OH)}\\ \mathrm{CMe{-}{-}{-}CO}\end{matrix}\right>\mathrm{O}}$$

No trace of the chloro-anhydride or acetyl-anhydride could be detected among the products formed in these reactions. The hydroxy-anhydride exhibits all the properties of the other members of the series; thus, when rapidly titrated it yields figures corresponding with those required for the hydroxy-pyrone, but the

neutral solution of the salt rapidly changes on keeping, yielding the monoalkali salt of the original acid:

$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CMe{:}C(OH)}\\ \mathrm{CMe{-}{-}{-}CO}\end{matrix}{>}\mathrm{O} \longrightarrow \mathrm{CMe}{<}\begin{matrix}\mathrm{CMe{:}C(OK)}\\ \mathrm{CMe{-}{-}{-}CO}\end{matrix}{>}\mathrm{O} \longrightarrow \mathrm{CMe}{<}\begin{matrix}\mathrm{CHMe{\cdot}CO_2K}\\ \mathrm{CMe{\cdot}CO_2K}\end{matrix}.$$

The Aniline Derivatives.—The behaviour of the $\alpha\beta\gamma$-trimethyl acid towards aniline is comparable with that of the $\alpha\gamma$-dimethyl acid, although it is evident that the presence of the methyl group on the β-carbon atom slightly increases the tendency for the mobile hydrogen atom to remain outside the three-carbon system; thus, when either the normal or hydroxy-anhydride is treated with aniline, the same semianilide is formed, and this compound when heated at 150° passes into the hydroxy-anil. The latter is also formed when the acid is heated with one molecular proportion of aniline at 150°. The tendency for the mobile hydrogen atom to pass back into the three-carbon system is, however, clearly shown by the fact that an alkaline solution of the hydroxy-anil slowly passes into the true anil and the semianilide, even at the ordinary temperature, and that the change is quickly completed if the solution is gently warmed. These reactions may therefore be represented in the following way:

$$\begin{matrix}\mathrm{CMe}{<}\begin{matrix}\mathrm{CMe{:}C(OH)}\\ \mathrm{CMe{-}{-}{-}CO}\end{matrix}{>}\mathrm{O} \longrightarrow \\ \\ \mathrm{CMe}{<}\begin{matrix}\mathrm{CHMe{\cdot}CO}\\ \mathrm{CMe{-}CO}\end{matrix}{>}\mathrm{O} \longrightarrow\end{matrix} \mathrm{CMe}{<}\begin{matrix}\mathrm{CMe{\cdot}CO{\cdot}NHPh}\\ \mathrm{CMe{\cdot}CO_2H}\end{matrix} \underset{\text{alkali}}{\overset{\text{heating}}{\rightleftarrows}}$$

$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CMe{:}C(OH)}\\ \mathrm{CMe{-}{-}{-}CO}\end{matrix}{>}\mathrm{NPh} \longrightarrow \mathrm{CMe}{<}\begin{matrix}\mathrm{CHMe{\cdot}CO}\\ \mathrm{CMe{-}CO}\end{matrix}{>}\mathrm{NPh}.$$

The derivatives of this acid which we have prepared are:

	Acid. (*cis*-form).	Normal anhydride.	Hydroxy-anhydride.	Hydroxy-anil.	Semi-anilide.	Anil.
$\alpha\beta\gamma$-Trimethylglutaconic Acid $\mathrm{CO_2H{\cdot}CMe{\cdot}CMe(H){\cdot}CMe{\cdot}CO_2H}$	127°	liquid	119°	103°	151°	162°

It is desirable to emphasise the following conclusions which may be drawn from the above experiments:

(1) The tendency for the mobile hydrogen atom to pass to a neighbouring carbonyl group is clearly shown by the α-monosubstituted derivatives of glutaconic acid as soon as ring-formation is effected (and the necessary carbonyl group supplied) by transforming the acids into their anhydrides.

(2) The increase in weight of the group occupying the α-position increases the tendency for the mobile hydrogen atom to remain outside the three-carbon system.

(3) This phenomenon cannot be illustrated by the aniline deriv-

ative of the α-monosubstituted acids, because the *cis*-semianilides are converted into stable *trans*-modifications at a lower temperature than that required to throw the mobile hydrogen atom out of the three-carbon system.

(4) The presence of a methyl group at the β-carbon atom considerably increases the tendency for the mobile hydrogen atom to remain outside the three-carbon system.

(5) The presence of methyl groups at both the α- and γ-carbon atoms increases the tendency for the hydrogen atom to remain within the three-carbon system.

(6) The conditions which tend to throw the mobile hydrogen atom outside the three-carbon system are also the conditions which confer stability on the *cis*-form of the acids.

(7) The less stable *cis*-forms can be prepared from the hydroxy-anhydrides in the presence of excess of strong alkali, as well as by the aid of an "anticatalyst" (casein).

Experimental.

The cis-*Forms of the α-Monosubstituted Glutaconic Acids with their Normal Anhydrides, Hydroxy-anhydrides, and Chloro-anhydrides.*

cis-*α-Methylglutaconic Acid and its Normal Anhydride.*—These compounds have been fully described by Feist and Pomme (*Annalen*, 1909, **370**, 61).

The Hydroxy-anhydride of α-Methylglutaconic Acid (6-*Hydroxy-3-methyl-α-pyrone*), $CH<\begin{matrix}CMe\text{——}CO\\CH{:}C(OH)\end{matrix}>O$.

This compound may be prepared by the distillation of the normal anhydride under diminished pressure, but is more easily obtained by heating the acid with twice the theoretical quantity of acetyl chloride in a sealed tube at 100° for six hours. The product, after evaporating the excess of acetyl chloride on the water-bath, consists of about equal proportions of the hydroxy-anhydride and the chloro-anhydride, which can be separated by dissolving the mixture in dry ether and shaking the solution with aqueous sodium hydrogen carbonate until the lower layer is alkaline. The deep magenta-red aqueous solution is then quickly acidified, and the oil which separates is extracted by shaking once with ether. The hydroxy-anhydride is purified by distilling the ethereal residue under diminished pressure. It may also be obtained free from the chloro-anhydride by boiling the acid with excess of acetic anhydride for two hours and distilling the product, but in this case the formation of highly-coloured by-products considerably diminishes the yield.

The hydroxy-anhydride boils at 167°/18 mm. as a colourless oil, which solidifies on cooling. It crystallises from benzene in long prisms, melting at 74·5°:

0·1570 gave 0·3260 CO_2 and 0·0655 H_2O. C=56·78; H=4·65.
$C_6H_6O_3$ requires C=57·1; H=4·7 per cent.

The hydroxy-anhydride is sparingly soluble in cold water, but dissolves on warming, yielding a solution from which the anhydride partly separates on cooling. It is, however, slowly converted by warm water into the *trans*-form of the α-methyl acid. It dissolves in sodium hydrogen carbonate solution with effervescence, yielding the monoalkali salt of the hydroxy-pyrone, but at the same time a partial change into the dialkali salt of the normal acid ensues, a fact which is clearly shown by the following titration, in which the anhydride was dissolved in excess of standard alkali and titrated back by hydrochloric acid:

0·1902 required 36·6 c.c. of NaOH solution (1 c.c.=0·0017 NaOH) for complete neutralisation. $C_6H_6O_3$ (monobasic) requires 35·34 c.c.*

The amount of alkali required for neutralisation increases with the time the alkaline solution of the salt is kept, and it is therefore evident that the change to the dialkali salt of the normal acid takes place fairly rapidly at the ordinary temperature. The neutral solution of the alkali salt of the hydroxy-pyrone formed in the above titration exhibits the characteristic property of all these substances of slowly developing a deep blue colour on keeping. This colour gradually changes through purple to red, and finally the solution becomes yellow. The silver salt of the monobasic acid, prepared through the ammonium salt, blackens almost at once.

The pure *cis*-form can be prepared by dissolving the anhydride in strong aqueous alkali, or by employing the "casein" method of Feist (compare *Annalen*, 1909, **370**, 52).

Oxidation.—The hydroxy-anhydride was oxidised in ice-cold alkaline solution by means of the requisite amount of permanganate. Oxalic acid was the only product which could be isolated.

The Chloro-anhydride of α-Methylglutaconic Acid (6-*Chloro-3-methyl-α-pyrone*), $CH{<}{\begin{matrix}CMe{\cdot}CO\\CH{=}CCl\end{matrix}}{>}O$.

The preparation of this compound has been partly described in the preceding section, since it remains in the ethereal solution after

* Better numbers can be obtained by dissolving the hydroxy-anhydride in cold alcohol and rapidly titrating with alkali direct; thus, 0·1712 required 31·9 c.c. of NaOH (1 c.c.=0·0017 NaOH); $C_6H_6O_3$ requires 31·8 c.c. (monobasic).

all the acid constituents have been extracted by alkali. It is also produced in considerable quantities when the α-methyl acid is boiled with excess of acetyl chloride on the water-bath for four hours. In this case, however, some normal anhydride accompanies the halogen derivative, but owing to the ease with which the latter substance crystallises, it can be readily isolated in a pure condition by spreading on a porous plate. The chloro-anhydride distils without decomposition at 130°/25 mm., and the distillate sets to a solid mass on cooling. It shows a most marked tendency to crystallise, and can be obtained from light petroleum (b. p. 50—60°) in long, colourless prisms, melting at 71°:

0·2351 gave 0·4285 CO_2 and 0·0728 H_2O. C = 49·70; H = 3·45.
0·2344 „ 0·2330 AgCl. Cl = 24·58.

$C_6H_5O_2Cl$ requires C = 49·8; H = 3·5; Cl = 24·6 per cent.

The chloro-anhydride is readily soluble in benzene, and can be distilled under the ordinary pressure without decomposition. It is remarkably stable towards boiling water, and a small quantity separates unchanged when the hot aqueous solution is cooled. It is readily volatile with steam, but is slowly hydrolysed by boiling water and more quickly by aqueous alkalis.

Owing to the hydrogen chloride generated in the former process the acid produced is entirely the *trans*-modification, but in the presence of excess of strong alkali the *cis*-form is alone obtained. The action of excess of aniline on the chloro-anhydride in benzene solution yields a precipitate of aniline hydrochloride. The residue obtained on evaporating the filtered benzene solution gives a solid substance when rubbed with dilute hydrochloric acid, which crystallises from dilute alcohol in small, colourless needles, melting at 158°:

The compound is insoluble in aqueous alkaline carbonates, and would therefore appear to be the *anilide* of the acid,

NHPh·CO·CMe·CH(H)·CH·CO·NHPh:

0·1216 gave 0·3252 CO_2 and 0·0713 H_2O. C = 73·04; H = 6·54.

$C_{18}H_{18}O_2N_2$ requires C = 73·5; H = 6·1 per cent.

The action of aniline on the chloro-anhydride under other conditions will be described in a future communication.

cis-α-*Ethylglutaconic Acid*, $CO_2H·CEt·CH(H)·CH·CO_2H$.

Since this acid is much more stable than the corresponding *cis*-modification of α-methylglutaconic acid, it can be readily prepared either from the chloro-anhydride and aqueous potassium hydroxide or from the hydroxy-anhydride with the same reagent, but in this case also the presence of hydrochloric acid causes a

complete conversion of the *cis-* into the *trans*-modifications, and when therefore the chloro-anhydride is boiled with water or when it is left for a long time in contact with moist air, the *trans*-form of the acid melting at 133—134° is alone formed. The *cis*-acid is best prepared in quantity by dissolving the hydroxy-anhydride in excess of strong alkali, adding *N*-hydrochloric acid until neutral, and then warming the solution on the water-bath for a few minutes until a test portion gives no precipitate of unaltered hydroxy-anhydride on the addition of acid. The solution is then acidified when quite cold, and extracted by ether. The acid crystallises from chloroform in small prisms, melting at 108°:

0·2091 gave 0·4055 CO_2 and 0·1148 H_2O. C = 52·90; H = 6·12.

$C_7H_{10}O_4$ requires C = 53·2; H = 6·3 per cent.

The *silver* salt is a white, curdy precipitate:

0·2571 gave 0·1492 Ag. Ag = 58·03.

$C_7H_8O_4Ag_2$ requires Ag = 58·06 per cent.

The *cis*-acid is fairly stable towards hydrochloric acid unless the mineral acid is generated *in situ*, as is the case when the chloro-anhydride is treated with water. It can be recrystallised from equal proportions of concentrated hydrochloric acid and water, but if boiled for some time with this mixture gradual conversion of the *cis-* into the *trans*-form ensues, and the change is usually complete after heating for thirty minutes. The acid is very stable toward alkalis, and it may be boiled for a considerable time with excess of alkali hydroxide without undergoing change.

The Normal Anhydride of cis-*α-Ethylglutaconic Acid,*

$$CH(H)<\begin{matrix}CEt\cdot CO\\ CH-CO\end{matrix}>O.$$

An attempt to prepare this substance by the action of acetyl chloride on the *cis*-acid yielded the hydroxy-anhydride as sole product. Ultimately the normal anhydride was prepared in small quantity by the action of phosphorus pentachloride on the *trans*-acid, the conditions employed being the same as those used by Feist and Pomme (*Annalen*, 1909, **370**, 69) for the preparation of the normal anhydride from *trans*-*α*-methylglutaconic acid. The anhydride is a liquid, insoluble in aqueous sodium hydrogen carbonate, and is completely converted into the hydroxy-anhydride on distillation under diminished pressure. It is therefore a matter of some difficulty to obtain this substance in a pure condition, but the following analysis was made of a specimen which had been purified by dissolving in ether and washing with sodium hydrogen carbonate solution:

0·1917 gave 0·4181 CO_2 and 0·1025 H_2O. C=59·49; H=5·94.
$C_7H_8O_3$ requires C=60·0; H=5·7 per cent.

The Hydroxy-anhydride of a-Ethylglutaconic Acid (6-*Hydroxy-3-ethyl-a-pyrone*), $CH{<}{\substack{CEt\text{——}CO\\CH{:}C(OH)}}{>}O$.

This compound is obtained, accompanied by the chloro-anhydride, by heating either the *cis*- or the *trans*-acid with twice the theoretical quantity of acetyl chloride in a sealed tube at 100° for six hours. The separation may be effected by evaporating the excess of chloride on the water-bath, dissolving the residue in pure ether, and shaking with aqueous sodium hydrogen carbonate until the lower layer is alkaline. The deep red alkaline solution deposits the anhydride as an oil when it is acidified, and this is then extracted by shaking once with ether. Some *cis*-acid, formed by the action of the alkali on the anhydride, is always extracted by this method, and it is therefore necessary to dissolve the ethereal residue in benzene, in which the *cis*-acid is quite insoluble, and filter in order to obtain the hydroxy-anhydride pure.

The anhydride distils as a mobile liquid at 176°/23 mm., and dissolves in aqueous sodium hydrogen carbonate with effervescence:

0·2313 gave 0·5052 CO_2 and 0·1146 H_2O. C=59·52; H=5·52.
$C_7H_8O_3$ requires C=60·0; H=5·7 per cent.

0·1540 required 36·8 c.c. of NaOH solution (1 c.c.=0·001193 gram NaOH) for complete neutralisation. $C_7H_8O_3$ (monobasic) requires 36·9 c.c.

It is evident, therefore, that the tendency for the mobile hydrogen atom to pass back into the three-carbon system is less with this compound than with the corresponding methyl derivative; in fact, the hydroxy-anhydride is almost completely recovered when the cold neutral solution is acidified. If, however, the neutral solution is boiled, the change to the mono-alkali salt of the *cis*-acid is rapidly effected. The neutral solution slowly becomes deep blue with violet fluorescence when kept, the colour changing first to red and then to yellow on further keeping. The hydroxy-anhydride is completely converted into the *trans*-acid when boiled with dilute hydrochloric acid.

The Chloro-anhydride of a-Ethylglutaconic Acid (6-*Chloro-3-ethyl-a-pyrone*), $CH{<}{\substack{CEt\text{—}CO\\CH{:}CCl}}{>}O$.

The ethereal solution, after extracting the hydroxy-anhydride in the experiment described above, yields the chloro-anhydride on

evaporating. It can also be formed from the *trans*-acid by boiling it with excess of acetyl chloride for four hours, and is isolated in the same manner as in the sealed-tube experiment. By either process the anhydride is obtained as a liquid, which distils at 133°/23 mm. as a colourless oil, solidifying to a mass of crystals on cooling. The solid melts sharply at 39° after being in contact with porous porcelain, but as it is readily soluble in all "inert" solvents it cannot be recrystallised:

0·1890 gave 0·1700 AgCl. Cl = 22·25.

$C_7H_7O_2Cl$ requires Cl = 22·4 per cent.

The chloro-anhydride dissolves slowly in excess of strong alkali hydroxide, the solution becoming warm and red in colour. When all oil has passed into solution the immediate addition of acid causes the separation of an oil free from halogen, which proved on examination to be the pure hydroxy-anhydride.

If the alkaline solution is allowed to remain until no oil is precipitated by acid, ether extracts the *cis*-acid from the acidified solution.

cis-*α-Benzylglutaconic Acid*, $CO_2H{\cdot}C(CH_2Ph){\cdot}CH(H){\cdot}CH{\cdot}CO_2H$.

This acid is readily prepared, either by dissolving the chloro-anhydride in potassium hydroxide solution and acidifying, or by boiling the hydroxy-anhydride with strong alkali (see p. 2226). In this case also the presence of hydrogen chloride formed *in situ* causes a complete conversion of the *cis*- into the *trans*-modification, and thus when the chloro-anhydride is boiled with water the acid of higher melting point is alone formed. When prepared by either of the above methods, the *cis*-acid separates from water in slender needles, melting at 139°:

0·1826 gave 0·4350 CO_2 and 0·0884 H_2O. C = 65·30; H = 5·39.

$C_{12}H_{12}O_4$ requires C = 65·5; H = 5·5 per cent.

The acid is more soluble in warm water than the *trans*-modification.

The *silver* salt is a crystalline solid:

0·2941 gave 0·1462 Ag. Ag = 49·71.

$C_{12}H_{10}O_4Ag_2$ requires Ag = 49·77 per cent.

The *cis*-acid is completely converted into the *trans*-modification when boiled for half an hour with concentrated hydrochloric acid. In strong alkaline solution it may be boiled for several hours without undergoing change.

The normal anhydride of α-benzylglutaconic acid could not be prepared. The acid and phosphorus pentachloride react very slowly, and ultimately yields a product containing much chlorine, from which no definite substance could be isolated.

The Hydroxy-anhydride of α-Benzylglutaconic Acid (6-*Hydroxy*-3-*benzyl-α-pyrone*), $CH{<}{}^{C(CH_2Ph)\cdot CO}_{CH{=\!=}C(OH)}{>}O$.

This substance is prepared by heating 5 grams of the *trans*-acid with 8 grams of acetyl chloride in a sealed tube at 100° for eight hours. The residue left on evaporating the excess of chloride yields the hydroxy-anhydride as a crystalline solid when rubbed with dry ether. It may be further purified by recrystallisation from a mixture of benzene and light petroleum (b. p. 50—60°), when it is obtained in long, flat needles, melting at 90°:

0·1444 gave 0·3748 CO_2 and 0·0634 H_2O. C = 71·02; H = 4·89.
$C_{12}H_{10}O_3$ requires C = 71·3; H = 5·0 per cent.

The *potassium* salt, $CH{<}{}^{C(CH_2Ph)\cdot CO}_{CH{=\!=}C(OK)}{>}O$, is precipitated in glistening plates when a slight excess of aqueous potassium hydroxide is added to a solution of the hydroxy-anhydride in the same alkali. It crystallises from absolute alcohol in brilliant leaflets:

0·1876 gave 0·0675 K_2SO_4. K = 16·13.
$C_{12}H_9O_3K$ requires K = 16·25 per cent.

The alcoholic filtrate becomes deep blue on keeping.

The following titration of the hydroxy-anhydride was made, the anhydride being dissolved in excess of standard alkali and titrated back with standard acid:

0·2004 required 33·45 c.c. of NaOH solution (1 c.c. = 0·001193 gram NaOH) for neutralisation. $C_{12}H_{10}O_3$ (monobasic) requires 33·26 c.c.

The neutral solution becomes deep blue on keeping. That the cause of this colour is the oxygen of the air is shown by shaking a warm solution of the potassium salt with free access of air, when a deep purple solution is formed, from which a blue precipitate separates on keeping. The dried precipitate closely resembles indigo in appearance, but dissolves in alcohol, forming a fine blue solution.

The *silver* salt is precipitated as a white powder, which blackens immediately, even in red light. A satisfactory analysis could not be obtained.

The hydroxy-anhydride may also be prepared from the chloro-anhydride by warming it with excess of aqueous potassium hydroxide, when the formation of the insoluble potassium salt of the hydroxy-acid enables this change to be easily followed. The stability of the hydroxy-anhydride is very considerable, and it is necessary to heat it with excess of alkali for at least half an hour

before conversion into the alkali salt of the *cis*-acid is complete. The end-point of this change can be easily determined, because the presence of any unaltered "enol" form causes the separation of the insoluble potassium salt when the solution is cooled.

When the hydroxy-anhydride is boiled with alcohol, it is quickly transformed into the acid ester of the dibasic acid; thus with ethyl alcohol, *ethyl hydrogen α-benzylglutaconate*,

$$CO_2H \cdot C(CH_2Ph) \colon CH \cdot CH_2 \cdot CO_2Et,$$

is formed, which crystallises from dilute alcohol in slender needles, melting at 93°:

0·1096 gave 0·2714 CO_2 and 0·0636 H_2O. C = 67·53; H = 6·46.

$C_{14}H_{16}O_4$ requires C = 67·8; H = 6·4 per cent.

Since the acid ester is hydrolysed to the *cis*-acid by potassium hydroxide it probably retains the *cis*-configuration.

When the hydroxy-anhydride is boiled with dilute hydrochloric acid (one part of concentrated hydrochloric acid to one of water) it passes into solution, and a crystalline solid separates on cooling, which melts fairly sharply at 125°. Since this substance behaves on titration as a dibasic acid, it is probably an equilibrium mixture of the *cis*- and *trans*-modifications. Prolonged boiling with the mineral acid yields the *trans*-modification as sole product.

The Chloro-anhydride of α-Benzylglutaconic Acid (6-*Chloro-3-benzyl-α-pyrone*), $CH \lessdot \begin{matrix} C(CH_2Ph) \cdot CO \\ CH = CCl \end{matrix} > O$.

The ethereal solution from the preparation of the hydroxy-anhydride described above contains the chloro-anhydride, together with a small quantity of dissolved hydroxy-anhydride. Separation can be effected by shaking the ethereal solution with dilute aqueous sodium hydrogen carbonate until the lower layer is alkaline. It is necessary to use the alkali dilute, because otherwise the separation of the sodium salt of the hydroxy-pyrone, which like the potassium salt is insoluble in excess of the reagent, causes difficulty in separating the two layers. The deep magenta alkaline washings deposit a further quantity of the hydroxy-anhydride when acidified. The dried ethereal solution leaves an oil on evaporation, which quickly becomes solid. When recrystallised by dissolving in hot light petroleum (b. p. 60—70°), and clearing when cooled by the addition of a little chloroform, it is obtained in long, slender needles, melting at 74°:

0·1934 gave 0·1258 AgCl. Cl = 16·09.

$C_{12}H_9O_2Cl$ requires Cl = 16·09 per cent.

The chloro-anhydride is readily soluble in benzene or chloroform.

When treated with strong aqueous potassium hydroxide, heat is generated, and the anhydride slowly passes into solution. At the same time the crystalline potassium salt of the hydroxy-anhydride separates.

The cis- *and* trans-*Semianilides of the α-Monosubstituted Glutaconic Acids.*

The trans-*Semianilide of α-Methylglutaconic Acid*,

$CO_2H\cdot CH_2\cdot CH\colon CMe\cdot CO\cdot NHPh$.

—Reference has been made in the introduction (p. 2213) to a difference in the result obtained by us and by Feist and Pomme respecting the behaviour of α-methylglutaconic acid towards aniline. The semianilide is produced in quantitative yield when the *trans*-acid, mixed with one molecular proportion of aniline, is heated at 150° for ten minutes, and is isolated by rubbing the product with pure ether. It crystallises from ethyl acetate in needle clusters, which melt at 189°, and lose carbon dioxide at 195°. The semianilide is soluble in aqueous sodium carbonate:

0·2167 gave 0·5220 CO_2 and 0·1129 H_2O. C=65·69; H=5·80.

$C_{12}H_{13}O_3N$ requires C=65·8; H=5·9 per cent.

0·2000 required 33·75 c.c. NaOH solution (1 c.c.=0·001079 gram NaOH) for complete neutralisation. $C_{12}H_{13}O_3N$ (monobasic) requires 33·86 c.c.

When the semianilide is heated until carbon dioxide has ceased to be evolved, the product is an oil insoluble in alkali. It was purified by dissolving in ether, and washing with dilute alkali. As the residue still showed no signs of solidifying and appeared to decompose on distillation, it was analysed:

0·2051 gave 0·5649 CO_2 and 0·1386 H_2O. C=75·11; H=7·51.

$C_{11}H_{13}ON$ requires C=75·4; H=7·4 per cent.

The numbers closely approximate to those required for the anilide, $CHMe\colon CMe\cdot CO\cdot NHPh$.

Oxidation of the Semianilide.—The oxidation was effected by dissolving the acid in sodium hydrogen carbonate solution and adding the calculated quantity of a solution of permanganate. The solution was then filtered, acidified, evaporated to dryness, and extracted in a Soxhlet apparatus with ether.

Malonic acid, melting at 132°, was obtained from the ethereal solution (Found, C=34·42; H=3·88. Calc., C=34·6; H=3·8 per cent.).

The trans-*Semianilide of α-Ethylglutaconic Acid*,

$CO_2H\cdot CH_2\cdot CH\colon CEt\cdot CO\cdot NHPh$.

—This substance is prepared in precisely the same manner as the

α-methyl derivative. It crystallises from dilute alcohol in needles, which melt at 170°, giving off carbon dioxide at 180°. The semianilide is soluble in aqueous sodium carbonate:

0·2096 gave 0·5137 CO_2 and 0·1181 H_2O. C=66·84; H=6·28.

$C_{13}H_{15}O_3N$ requires C=66·9; H=6·4 per cent.

The trans-*Semianilide of α-Benzylglutaconic Acid*,
$CO_2H{\cdot}CH_2{\cdot}CH{:}C(CH_2Ph){\cdot}CO{\cdot}NHPh$.
—The preparation of this compound is the same as described in the case of the α-methyl derivative. It crystallises from dilute alcohol in small needles, which melt at 175°, and evolve carbon dioxide at 190°:

0·1846 gave 0·4965 CO_2 and 0·0955 H_2O. C=73·35; H=5·76.

$C_{18}H_{17}O_3N$ requires C=73·2; H=5·8 per cent.

The *cis*-semianilides are prepared by the action of aniline on the hydroxy-anhydrides. They pass into the *trans*-semianilides when heated at 150°.

The cis-*Semianilide of α-Methylglutaconic Acid*,
$CO_2H{\cdot}CH_2{\cdot}CH{:}CMe{\cdot}CO{\cdot}NHPh$.
—When a solution of the hydroxy-anhydride of α-methylglutaconic acid in benzene is mixed with a benzene solution of the requisite quantity of aniline, heat is generated, and the solution becomes deep magenta-red. At the same time a solid substance separates, which is collected and rubbed with pure ether. The semianilide crystallises from dilute alcohol in slender needles, which melt at 148°, evolving carbon dioxide at a higher temperature:

0·1461 gave 0·3509 CO_2 and 0·0797 H_2O. C=65·60; H=6·08.

$C_{12}H_{13}O_3N$ requires C=65·8; H=5·9 per cent.

The semianilide is readily soluble in aqueous sodium carbonate. When it is heated at 150° for twenty minutes, transformation into the *trans*-semianilide is complete. The compound may be isolated by rubbing the product with ether.

The cis-*Semianilide of α-Ethylglutaconic Acid*,
$CO_2H{\cdot}CH_2{\cdot}CH{:}CEt{\cdot}CO{\cdot}NHPh$.

—Since this semianilide is soluble in benzene it does not separate when a benzene solution of the hydroxy-anhydride is mixed with a benzene solution of aniline. It may be isolated, however, by evaporating the solution free from benzene, adding ether, and shaking with aqueous sodium carbonate. The oil which separated on acidifying the alkaline solution set to a solid mass, and was purified by rubbing with dry ether and recrystallising from dilute alcohol. The product obtained in this manner did not melt sharply; it was therefore rubbed with benzene, and filtered from a small quantity

of insoluble material. The residue from the benzene filtrate was then recrystallised from dilute alcohol, and obtained in silky needles, melting at 121°:

0·1428 gave 0·3495 CO_2 and 0·0845 H_2O. C=67·01; H=6·59.

$C_{13}H_{15}O_3N$ requires C=66·9; H=6·4 per cent.

The portion insoluble in benzene proved to be the *trans*-semianilide melting at 170°, and it is therefore evident that even at the temperature of the water-bath some conversion of the *cis*- into the *trans*-modification had taken place. This change is complete when the *cis*-semianilide is heated at 150° for fifteen minutes.

The Semianilide from the Normal Anhydride of α-Ethylglutaconic Acid, $CO_2H·CH\colon CH·CHEt·CO·NHPh$.—This substance is prepared by the action of aniline on the normal anhydride in benzene solution, and is isolated by extracting the ethereal solution of the residue with aqueous sodium carbonate. It crystallises from dilute alcohol in small plates, melting at 149°:

0·1499 gave 0·3666 CO_2 and 0·0884 H_2O. C=66·75; H=6·55.

$C_{13}H_{15}O_3N$ requires C=66·9; H=6·4 per cent.

The cis-*Semianilide of α-Benzylglutaconic Acid*,

$CO_2H·CH_2·CH\colon C(CH_2Ph)·CO·NHPh$.

—In this case the semianilide separates when benzene solutions of the hydroxy-anhydride and aniline are mixed. It crystallises from dilute alcohol in long, slender needles, melting at 143°. The semianilide dissolves in aqueous sodium carbonate, but if the alkali is strong an oily sodium salt is precipitated, which, however, dissolves when water is added:

0·2042 gave 0·5451 CO_2 and 0·1022 H_2O. C=73·00; H=5·57.

$C_{18}H_{17}O_3N$ requires C=73·2; H=5·8 per cent.

The *cis*-semianilide is completely converted into the *trans*-semianilide, melting at 175°, when heated at 150° for fifteen minutes.

The Normal Anhydrides, Hydroxy-anhydrides, and Chloro-anhydrides of the Disubstituted Glutaconic Acids.

αβ-Dimethylglutaconic Acid.—We have been unable to prepare the normal anhydride of this acid. The tendency for the mobile hydrogen atom to pass outside the three-carbon system is so considerable that even when dehydration is effected at low temperatures the hydroxy-anhydride is alone formed.

The Hydroxy-anhydride of $\alpha\beta$*-Dimethylglutaconic Acid* (6-*Hydroxy*-3:4-*dimethyl*-α-*pyrone*), $CMe<\begin{matrix}CMe\text{---}CO\\CH:C(OH)\end{matrix}>O$.

This substance is formed by the action of boiling acetyl chloride on the acid, and was described in a former communication (Trans., 1905, **87**, 1696) as the normal anhydride. It is a mobile liquid, which boils at 183°/25 mm. (through a misprint the boiling point was wrongly given in the original paper):

0·1629 required 38·9 c.c. of NaOH solution (1 c.c. = 0·001193 gram NaOH) for complete neutralisation. $C_7H_8O_3$ (monobasic) requires 39·0 c.c.

The hydroxy-anhydride is precipitated by adding acid to a solution of the anhydride in alkali, and the change into the alkali salt of the dibasic acid is very slow at the ordinary temperature. The acid formed is the same as that from which the anhydride was derived. The neutral solution from the above titration becomes deep purple on keeping, and it is evident that the property of forming coloured solution in this manner is characteristic of all hydroxy-anhydrides.

The Acetyl-anhydride of $\alpha\beta$*-Dimethylglutaconic Acid* (6-*Acetoxy*-3:4-*dimethyl*-α-*pyrone*), $CMe<\begin{matrix}CMe\text{---}CO\\CH:C(OAc)\end{matrix}>O$.

It is possible to isolate this substance in a pure condition because there is no tendency whatever for the production of the chloro-anhydride when the acid is heated with acetyl chloride at the temperature of the boiling reagent. The acid is heated with a large excess of acetyl chloride for six hours on the water-bath, and the excess of the chloride is then evaporated. The neutral acetyl-anhydride is separated from the hydroxy-anhydride by dissolving the residue in ether and shaking with aqueous sodium hydrogen carbonate, and is obtained as a crystalline solid when the ethereal solution is evaporated. It crystallises from a mixture of chloroform and light petroleum (b. p. 50—60°) in long, rhombic prisms, melting at 65°:

0·2385 gave 0·5189 CO_2 and 0·1202 H_2O. C = 59·33; H = 5·60.

$C_9H_{10}O_4$ requires C = 59·3; H = 5·5 per cent.

The acetyl-anhydride is readily soluble in benzene or chloroform; it is insoluble in light petroleum. When warmed with aqueous potassium hydroxide it slowly dissolves, and a crystalline potassium salt separates if a sufficient excess of alkali is present. The solution of this salt in water when acidified yields the acid melting at 148°.

The constitution of the acetyl-anhydride was proved by the formation of acetanilide by the action of aniline. The anhydride dissolved in benzene was mixed with a benzene solution containing excess of aniline, and the mixture evaporated free from the solvent. The residue was then dissolved in ether, and shaken, first with sodium carbonate solution and then with dilute hydrochloric acid. Acetanilide (m. p. 115°) was isolated from the ethereal solution on evaporation (Found, C = 70·92; H = 6·81. Calc., C = 71·1; H = 6·7 per cent.). When the sodium carbonate washings from the above preparation are acidified, the semianilide melting at 139° (see p. 2218) is precipitated.

The Chloro-anhydride of αβ-Dimethylglutaconic Acid (6-*Chloro*-3:4-*dimethyl-α-pyrone*), $CMe<\begin{matrix}CMe\cdot CO\\CH:CCl\end{matrix}>O$.

This substance is prepared in small amount by heating αβ-dimethylglutaconic acid with twice the theoretical amount of acetyl chloride in a sealed tube at 100° for ten hours, and can be isolated in the same way as the chloro-anhydrides already described. It is a liquid which distils at 133°/26 mm.:

0·2069 gave 0·1872 AgCl. Cl = 22·37.

$C_7H_7O_2Cl$ requires Cl = 22·4 per cent.

The chloro-anhydride slowly dissolves when shaken with aqueous potassium hydroxide, and the solution, when acidified and extracted by ether, yields the acid melting at 148°.

The Normal Anhydride of αγ-Dimethylglutaconic Acid,

$$CH(H)<\begin{matrix}CMe\cdot CO\\CMe\cdot CO\end{matrix}>O.$$

When 5 grams of αγ-dimethylglutaconic acid are heated on the water-bath with 40 c.c. of acetyl chloride, a vigorous reaction ensues, and much hydrogen chloride is evolved. The reaction ceases after thirty minutes, and the anhydride can be isolated by evaporating the chloride, dissolving the residue in ether, and shaking the ethereal solution with aqueous sodium hydrogen carbonate. The oil obtained from the ethereal solution on evaporation slowly polymerises to a resin when kept in an evacuated desiccator; as, moreover, it passed into the hydroxy-anhydride (q.v.) and other products when distilled, it was analysed after it had been kept in a vacuum for two hours. The hydrogen result is therefore rather high, owing to the presence of traces of ether:

0·2290 gave 0·5042 CO_2 and 0·1241 H_2O. C = 60·05; H = 6·02.

$C_7H_8O_3$ requires C = 60·0; H = 5·7 per cent.

The anhydride is insoluble in cold aqueous sodium carbonate, but slowly dissolves on warming. The acid melting at 147° is extracted from the acidified solution by ether.

The Hydroxy-anhydride of αγ-Dimethylglutaconic Acid (6-*Hydroxy*-3:5-*dimethyl-α-pyrone*), $CH{<}{}^{CMe\text{---}CO}_{CMe:C(OH)}{>}O$.

The hydroxy-anhydride is readily prepared by heating the normal anhydride at 150° for ten minutes, and can be isolated by dissolving the melted product in ether, and shaking with aqueous sodium hydrogen carbonate. The alkaline solution, if immediately acidified, precipitates the anhydride as an oil, which quickly becomes solid. It is also formed, accompanied by some chloro-anhydride, when αγ-dimethylglutaconic acid is heated with twice the theoretical amount of acetyl chloride in a sealed tube at 100° for six hours, and can be separated by the method already described. The anhydride distils at 183°/27 mm. as a mobile oil, which solidifies on cooling. It crystallises from a mixture of benzene and light petroleum (b. p. 60—70°) in glistening plates, melting at 75°:

0·2244 gave 0·4922 CO_2 and 0·1144 H_2O. C=59·81; H=5·66.

$C_7H_8O_3$ requires C=60·0; H=5·7 per cent.

The hydroxy-anhydride is readily soluble in benzene, sparingly so in ether, and practically insoluble in light petroleum. It dissolves in aqueous sodium hydrogen carbonate with effervescence, and can be partly recovered if the solution is quickly acidified, but if kept at the ordinary temperature for twenty minutes it is completely converted into the salt of the acid from which it was derived; this can be recovered by extracting the acidified solution with ether:

0·1537 required 36·7 c.c. NaOH solution (1 c.c.=0·001192 gram NaOH) for complete neutralisation. $C_7H_8O_3$ (monobasic) requires 36·8 c.c.

The usual purple colour is developed when the neutral solution is kept.

The hydroxy-anhydride dissolves when boiled with water, and on cooling a small amount separates unaltered. It is, however, rapidly converted by hot water into αγ-dimethylglutaconic acid.

The Chloro-anhydride of αγ-Dimethylglutaconic Acid (6-*Chloro*-3:5-*dimethyl-α-pyrone*), $CH{<}{}^{CMe-CO}_{CMe:CCl}{>}O$.

A compound to which the above formula was assigned was prepared by Feist and Reuter (*Annalen*, 1909, **370**, 82) by the action of phosphorus pentachloride on αγ-dimethylglutaconic acid,

but only in very small quantity. It can be prepared in a yield of about 30 per cent. by heating $\alpha\gamma$-dimethylglutaconic acid with twice the theoretical quantity of acetyl chloride in a sealed tube at 100° for eight hours, and can be isolated in the usual manner. The compound melts at 82—83°, as described by Feist and Reuter. (Found, Cl = 22·31. Calc., Cl = 22·4 per cent.)

The chloro-anhydride slowly dissolves when warmed with aqueous potassium hydroxide, and the solution when acidified and extracted with ether yields $\alpha\gamma$-dimethylglutaconic acid, melting at 147°.

The Semianilides, Hydroxy-anils, and Anils of the Disubstituted Glutaconic Acids.

The Semianilide of $\alpha\beta$-Dimethylglutaconic Acid, $CO_2H{\cdot}CMe{:}CMe{\cdot}CH_2{\cdot}CO{\cdot}NHPh$.—This substance, which melts at 139°, was described in a former paper (Trans., 1905, **87**, 1697). When heated at 150° it loses water, and is converted into the hydroxy-anil. The same semianilide is formed from the anhydride, both before and after distillation.

The Hydroxy-anil of $\alpha\beta$-Dimethylglutaconic Acid (3-*Hydroxy*-2-*phenyl*-5 : 6-*dimethyl*-1 : 2-*dihydropyridone*),

$$CMe{<}{\begin{matrix}CMe\text{---}CO\\ CH{:}C(OH)\end{matrix}}{>}NPh.$$

This compound can be prepared either by heating the semianilide in the manner described above, or by heating $\alpha\beta$-dimethylglutaconic acid with one molecular quantity of aniline at 150° for fifteen minutes. In both cases the product is isolated by rubbing with pure ether, in which the hydroxy-anil is insoluble. It crystallises from alcohol in lustrous plates, melting at 125°:

0·1281 gave 0·3391 CO_2 and 0·0707 H_2O. C = 72·25; H = 6·15.
0·1276 „ 0·3383 CO_2 „ 0·0675 H_2O. C = 72·30; H = 5·90.
$C_{13}H_{13}O_2N$ requires C = 72·6; H = 6·1 per cent.

0·2087 required 36·5 c.c. of NaOH solution (1 c.c. = 0·001072 gram NaOH). $C_{13}H_{13}O_2N$ (monobasic) requires 36·3 c.c.

The dissociation of the salt of the hydroxy-anil (see p. 2220) causes the neutral solution to become alkaline on keeping, but the further addition of 0·2 c.c. of $N/10$-acid is sufficient to stop this process, and therefore the amount of anil formed is too small to be isolated.

The neutral solution of the alkali salt can be boiled for some considerable time without undergoing change, and it is therefore evident that the condition having the mobile hydrogen atom outside the three-carbon system possesses remarkable stability.

The Semianilide of $\alpha\gamma$-Dimethylglutaconic Acid,
$CO_2H{\cdot}CMe{:}CH{\cdot}CHMe{\cdot}CO{\cdot}NHPh$.
—This compound can be prepared either from the normal anhydride or the hydroxy-anhydride by dissolving in benzene and adding a benzene solution containing rather more than the requisite amount of aniline. It can be isolated by evaporating free from the solvent, dissolving in ether, and shaking the ethereal solution with aqueous sodium carbonate. The semianilide separates from dilute alcohol in microscopic needle clusters, melting at 165—166°:

0·1883 gave 0·4604 CO_2 and 0·1130 H_2O. C = 66·68; H = 6·68.
$C_{13}H_{15}O_3N$ requires C = 66·9; H = 6·4 per cent.

When the semianilide is prepared from the hydroxy-anhydride some neutral substance remains in the ethereal solution, which crystallises from alcohol in small needles, melting at 195°, and is probably the *anilide* of *$\alpha\gamma$-dimethylglutaconic acid*,
$NHPh{\cdot}CO{\cdot}CMe{:}CH{\cdot}CHMe{\cdot}CO{\cdot}NHPh$:

0·2297 gave 0·6215 CO_2 and 0·1337 H_2O. C = 73·77; H = 6·49.
$C_{19}H_{20}O_2N_2$ requires C = 74·0; H = 6·5 per cent.

When the semianilide is heated at 150° for fifteen minutes it is completely transformed into the hydroxy-anil and water.

The Hydroxy-anil of $\alpha\gamma$-Dimethylglutaconic Acid (3-*Hydroxy*-2-*phenyl*-4 : 6-*dimethyl*-1 : 2-*dihydropyridone*),

$$CH{<}\begin{matrix}CMe\text{——}CO\\CMe{:}C(OH)\end{matrix}{>}NPh.$$

After several experiments on the action of aniline on $\alpha\gamma$-dimethylglutaconic acid it was found that the best yield of the hydroxy-anil was obtained by boiling the acid with excess of aniline for one hour. The product can be isolated by pouring the aniline solution into dilute hydrochloric acid, extracting the insoluble oil by ether, and shaking the ethereal solution with aqueous sodium carbonate.* It crystallises from dilute alcohol in plates, melting at 112°:

0·2046 gave 0·5425 CO_2 and 0·1107 H_2O. C = 72·32; H = 6·03.
$C_{13}H_{13}O_2N$ requires C = 72·6; H = 6·1 per cent.

0·1935 required 33·4 c.c. of NaOH solution (1 c.c. = 0·001072 gram NaOH) for neutralisation. $C_{13}H_{13}O_2N$ (monobasic) requires 33·6 c.c.

The indicator colour of the neutral solution (phenolphthalein) slowly returns on keeping, and it is possible to add 2·3 c.c. of *N*/10-acid before this process ceases. By using larger quantities the crystalline precipitate which separates from the neutral solution on

* A small quantity of the normal anil is always formed by this method, but is removed on crystallisation.

keeping can be collected. It crystallises from alcohol, in which it is sparingly soluble, in small needles, melting at 174°, forming a magenta-red liquid:

0·2025 gave 0·5381 CO_2 and 0·1096 H_2O. C = 72·48; H = 6·02.

$C_{13}H_{13}O_2N$ requires C = 72·6; H = 6·1 per cent.

The compound is therefore the *anil* of *αγ-dimethylglutaconic acid*, $CH(H)<\begin{matrix}CMe\cdot CO\\CMe\cdot CO\end{matrix}>NPh$. When a neutral solution of the hydroxy-anil is acidified, the substance is precipitated unaltered, but if the neutral solution is warmed on the water-bath for half an hour and then acidified, the semianilide melting at 165—166° is precipitated. The following analysis and titration was made of this product in order to place its identity beyond question. (Found, C = 66·67; H = 6·34. Calc., C = 66·9; H = 6·5 per cent.):

0·2004 required 31·9 c.c. of NaOH solution (1 c.c. = 0·001079 gram NaOH) for neutralisation. $C_{13}H_{15}O_3N$ requires 31·88 c.c.

The colour of the indicator does not return when the neutral solution is kept. The semianilide is reconverted into the hydroxy-anil when heated at 150°.

The Normal Anhydrides and Hydroxy-anhydrides of the Trisubstituted Glutaconic Acids.

The only acid belonging to this series which we have as yet investigated is αβγ-trimethylglutaconic acid. (For method of preparation compare Trans., 1905, **87**, 1704.)

The Normal Anhydride of αβγ-Trimethylglutaconic Acid,

$$CMe(H)<\begin{matrix}CMe\cdot CO\\CMe\cdot CO\end{matrix}>O.$$

This substance can be prepared by heating the acid with excess of acetyl chloride on the water-bath for one hour, and can be isolated by evaporating the reagent, dissolving the residue in ether, and extracting acid impurities by shaking with aqueous sodium hydrogen carbonate. It is a liquid which passes into the hydroxy-anhydride on distillation. It does not, however, show any tendency to polymerise, and can therefore be purified by placing in an evacuated desiccator for twelve hours:

0·1992 gave 0·4556 CO_2 and 0·1222 H_2O. C = 62·38; H = 6·81.

$C_8H_{10}O_3$ requires C = 62·3; H = 6·5 per cent.

The high content of hydrogen can be accounted for by the presence of traces of dissolved ether.

The Hydroxy-anhydride of αβγ-Trimethylglutaconic Acid
(*6-Hydroxy-*3:4:5-*trimethyl-α-pyrone*),

$$CMe<\begin{matrix}CMe\text{——}CO\\CMe{:}C(OH)\end{matrix}>O.$$

This compound was described as the normal anhydride in the previous paper (Trans., 1905, **87**, 1705). It can be prepared either by the method then given or by heating the normal anhydride at 150° for fifteen minutes. The melting point is 119°, as stated previously. The anhydride is fairly stable in the presence of excess of alkali, but is best titrated directly with alkali in very cold dilute alcoholic solution. The figures are, however, only approximate:

0·1897 required 41·6 c.c. of NaOH solution (1 c.c. = 0·001176 gram NaOH) for neutralisation. $C_8H_{10}O_3$ (monobasic) requires 41·07 c.c.

When the hydroxy-anhydride is dissolved in alkali, no precipitate of unchanged material occurs on the addition of acid, and it is evident that even at the ordinary temperature transformation into the salt of the dibasic acid is fairly rapid. The acid formed either directly or in the presence of casein in accordance with Feist's method is the same acid as that from which the anhydride was derived.

The formation of the chloro-anhydride by the prolonged action of acetyl chloride on αβγ-trimethylglutaconic acid was not observed.

The Semianilide and Hydroxy-anil of the Trisubstituted Glutaconic Acid.

The Semianilide of αβγ-Trimethylglutaconic Acid,
$CO_2H{\cdot}CMe{:}CMe{\cdot}CHMe{\cdot}CO{\cdot}NHPh$.
—The same semianilide is prepared both from the normal anhydride and hydroxy-anhydride when they are treated in benzene solution with the requisite amount of aniline dissolved in the same solvent. The product is isolated by evaporating the solvent, and shaking the ethereal solution of the residue with aqueous sodium carbonate. It crystallises from dilute alcohol in slender needles, melting at 151°:

0·2100 gave 0·5223 CO_2 and 0·1317 H_2O. C = 67·83; H = 6·97.
$C_{14}H_{17}O_3N$ requires C = 68·0; H = 6·9 per cent.

The semianilide is completely converted into the hydroxy-anil when heated at 150° for fifteen minutes. It is readily soluble in benzene or alcohol.

The Hydroxy-anil of αβγ-Trimethylglutaconic Acid (3-*Hydroxy-2-phenyl*-4:5:6-*trimethyl*-1:2-*dihydropyridone*),

$$CMe{<}{\begin{matrix}CMe{-\!-\!-}CO\\CMe{:}C(OH)\end{matrix}}{>}NPh.$$

This compound is best prepared by heating the acid with one molecular quantity of aniline for fifteen minutes at 150°. The product is completely soluble in ether, and therefore the hydroxy-anil must be isolated by shaking the ethereal solution with aqueous sodium carbonate. It crystallises from dilute alcohol in small needles, melting at 103°:

0·1435 gave 0·3834 CO_2 and 0·0824 H_2O. C = 73·04; H = 6·40.
$C_{14}H_{15}O_2N$ requires C = 73·4; H = 6·6 per cent.

In this experiment the sodium carbonate extract must be acidified immediately, otherwise some semianilide is formed. The following titration was made by dissolving the hydroxy-anil in dilute alcohol, and titrating direct with alkali:

0·1621 required 24·0 c.c. NaOH solution (1 c.c. = 0·001174 gram NaOH) for neutralisation. $C_{14}H_{15}O_2N$ requires 24·1 c.c.

When the neutral solution is warmed and then acidified, the semianilide melting at 151° is precipitated on acidifying.

When the hydroxy-anil is dissolved in excess of cold alkali and the solution is titrated with standard acid until neutral, the colour of the indicator (phenolphthalein) returns on keeping. A small amount of crystalline material is obtained by adding acid until the solution remains neutral. This is the *anil* of *αβγ-trimethylglutaconic acid*, $CMe(H){<}{\begin{matrix}CMe{\cdot}CO\\CMe{\cdot}CO\end{matrix}}{>}NPh$, and separates from alcohol in slender needles, melting at 162°:

0·1562 gave 0·4186 CO_2 and 0·0906 H_2O. C = 73·08; H = 6·38.
$C_{14}H_{15}O_2N$ requires C = 73·4; H = 6·6 per cent.

The amount of the anil formed in this manner is very small, as the greater portion of the hydroxy-anil is converted into the semianilide during the course of the experiment.

THE SORBY RESEARCH LABORATORY,
THE UNIVERSITY, SHEFFIELD.

CCXLIX.—*Electromotive Forces in Alcohol. Part II. The Hydrogen Electrode in Alcohol and the Influence of Water on its Electromotive Force.*

By Robert Taylor Hardman and Arthur Lapworth.

It is generally stated that the electromotive force obtained when two platinum sheets saturated with hydrogen are immersed in two dilute aqueous solutions, which are in mutual contact, is given by the expression:

$$E = \frac{RT}{F}\log_e\frac{C}{C'},$$

(where C and C' represent the concentrations of the "hydrogen ions" in the two liquids respectively, and E, R, T, and F have their usual significance), provided that there is no potential difference at the liquid boundary, and that there is no substance present which can be reduced by the hydrogen under the experimental conditions.

The quantities C and C' in the foregoing expression properly refer to those hydrions which are characteristic of aqueous solutions of acids rather than to the "free" hydrogen ions. Nevertheless, the equation is equally true in either sense, as in any given basic solvent the active mass of the latter is nearly constant, and consequently the ratio:

[solvated hydrions]/[free hydrions]

is constant for univalent ions at any fixed temperature. In such cases as the above relations hold, it is also true that:

availability of acid/[solvated hydrions]

is a constant; hence the electromotive force of the concentration cell is also given by:

$$E = \frac{RT}{F}\log_e\frac{P}{P'},$$

where P and P' are the availabilities of the acid in the two liquids (Trans., 1908, **93**, 2203, and 1910, **97**, 21).

As all the foregoing relations have a sound thermodynamic basis, the question whether "free" hydrogen ions actually exist in such solutions is immaterial at least when passing from the first expression for E to the second, the sole assumptions made being that the gas laws are applicable to the ions, and that the current production is conceived as taking place in a truly reversible manner. The supposition that the elementary hydrogen at the electrodes passes into solution as "free" hydrogen ions is not a necessary part of the

proof, as the same result is obtained if it be supposed that the process occurring at the electrodes is the direct formation of the solvated ions, as, for example:

$$H_2O + \tfrac{1}{2}H_2 \rightleftharpoons H\cdot H_2O^{\cdot} + \ominus,$$

when the free energy relations of these ions are similar to those usually associated with the "free" hydrogen ions. The ionic solution pressure must then be considered as due to the same reaction.

The formula which shows the connexion between the potential and the availabilities of the acid in the cell compartments is of more general applicability than the one first given, as it is not restricted to cases in which the solvent itself forms complex hydrions. As the only solvents hitherto investigated from this point of view come under the latter category, a general thermodynamic proof of the availability formula, although comparatively simple, is at present hardly necessary.

Occasion may be taken to point out that numerous experiments on alcoholic solutions of mineral acids show that the law of mass action holds as nearly true for such solutions as for aqueous ones. Consequently, the restrictions under which the foregoing formulæ are applied are not here appreciably more serious with the one solvent than with the other.

It has already been shown that the anticatalytic effect of water on solutions of mineral acids in organic solvents can readily be accounted for on the view that water behaves as a weak base, so that when it is added to such solutions the concentration of the "free" hydrogen ions is diminished, or the availability of the acid is depressed, and experimental proof of a direct connexion between the catalytic activity and the salt-forming power of hydrogen chloride in alcohol was adduced. In experiments described in the present paper the theory has been put to a further test by ascertaining the electromotive forces obtained with concentration cells containing alcoholic hydrogen chloride as cell liquid, and having electrodes reversible to hydrogen ions.

Preliminary experiments were made with solutions of hydrogen chloride without any subsidiary electrolyte to minimise the potential differences at the liquid boundary, and it was found that with suitable precautions consistent electromotive forces were registered which could be reproduced within less than a millivolt.

The results with solutions having different concentrations of acid in the two compartments were in fairly good agreement with the high value for the transport number of chloridion deduced by other means (Lapworth and Partington, this vol., p. 1420), when neither solution had a concentration of hydrogen chloride much less than $N/10$. With solutions of concentrations considerably less than

$N/10$, consistent and reproducible electromotive forces were again obtained, but these were almost invariably smaller than those anticipated, by several millivolts, and although various explanations suggest themselves, these cannot at present be tested; additional experiments will be undertaken in the hope of explaining this discrepancy.

Having convinced themselves that sharp and consistent results could be obtained with anhydrous alcoholic solutions, the authors then proceeded to examine what was the effect of the addition of small quantities of pure water to either solution, and observed that when the addition was made to the stronger solution a fall in the electromotive force occurred, whilst if it was made to the weaker solution an increase in the electromotive force occurred.

Quantitative experiments were then carried out, in most cases with solutions of equal concentrations of hydrogen chloride in both cells and with varying quantities of water in one cell only. The influence of small quantities of water was more marked the lower the concentration of acid, an effect which at least in part may be explained by the fact that the active mass of the free water is naturally less in the stronger solutions, as a more considerable part of that which has been added is removed by combination with the hydrogen chloride. With the highly dilute solutions observations were made only with great difficulty, as was to be expected, but with frequent repetition fairly satisfactory records were made.

In these cases any exact interpretation of the results is somewhat difficult, if not impossible, owing to uncertainties in estimating the potential of the liquid boundary. It may be regarded as safe to assume that this is in most cases of relatively small magnitude. The results of Baly, Burke, and Marsden (Trans., 1909, **95**, 1100) show that such small quantities of water affect the degree of dissociation of alcoholic hydrogen chloride to but a relatively small extent, and the same statement applies to the molecular conductivity of such solutions, so that the boundary potential resulting from the interdiffusion of the ions in the two liquids can have only a secondary importance.

The most satisfactory results of all, however, were obtained with highly dilute solutions of hydrogen chloride in presence of lithium chloride as a subsidiary electrolyte. It was found that if the two cells were filled with an alcoholic solution of this salt, and small quantities of water were added to one of the cells, no definite potential difference could be detected when the apparatus was working in the usual manner. In presence of very dilute hydrogen chloride, however, very considerable electromotive forces were registered, which were easily measured, constant and reproducible.

With the more highly dilute solutions of acid the fall in availability due to the addition of water was in close accordance with the formula:

$$\frac{P'}{P}=\frac{r}{r+w}$$

where P' is the availability of the acid in the moist solution, P that of the acid in anhydrous alcohol, w being the concentration of the water in gram-molecules per litre, and r a constant (compare Trans., 1910, **97**, 22). On calculating r by means of this formula for the separate observations, it was found to decrease rapidly with the amount of water present in the stronger solutions, less rapidly with the weaker ones, and always approaching a value 0·122, which was reached with $N/500$-hydrogen chloride in presence of lithium chloride.

It has been shown in previous papers already referred to, that the availability of this acid as measured by its activity in accelerating the esterification of an acid, or by its power of forming salts with a weak base, may be represented by a formula identical with the above, the value of r approximating to 0·1 at 25° (compare, in particular, Trans., 1910, **97**, 22 *et seq.*). Goldschmidt and Udby, on the other hand, obtained results from measurements of the velocity of the esterification of numerous acids, indicating that the speed is proportional to $1/r+w$ if the value 0·15 be assigned to r (*Zeitsch. physikal. Chem.*, 1907, **60**, 735 *et seq.*), so that the discrepancies between results obtained by entirely different methods are not greater than those between values deduced by different observers when using the same method. The relatively small magnitude of the divergence will be clear when it is realised that the presence of less than one-tenth per cent. of water in the alcohol would be sufficient to cause a variation of the same magnitude as is seen in the extreme values hitherto assigned to r at 25°, although it is highly improbable that this is the origin of the discrepancies, which may perhaps be traced when more refined methods have been developed.

The results so far obtained appear to offer unequivocal support for the solvate theory for highly ionised acids, and the expression:

$$(C_2H_6O,H)^{\cdot}+H_2O=(H_2O,H)^{\cdot}+C_2H_6O,$$

put forward for the first time by Goldschmidt and Udby as the basis of an explanation of the depressant effect of water on the catalytic activity of acids in promoting esterification, may, if interpreted broadly, be regarded as representing the equilibrium in a highly dilute solution of an acid in moist alcohol. Applied with this reservation and solely to those cases of catalysis and salt formation known to be due exclusively, or nearly so, to reactions

of complex hydrions, the solvate theory renders unnecessary, at least for the present, theories such as that of Reid (*Amer. Chem. J.*, 1909, **41**, 499 *et seq.*), where changes in the viscosity of the medium are suggested as one of the principal causes of the anticatalytic influence of water on organic media.

The results of Tubant and his colleagues, obtained by measurements of the speed of inversion of menthone by acids in alcoholic solution (*Annalen*, 1910, **377**, 284 *et seq.*), suggest that this reaction is not so nearly exclusively ionic in character as is ordinary accelerated esterification, for the velocities of reaction are not even roughly proportional to the "hydrogen ion" concentration in absolute alcohol as measured by the degree of ionisation of the catalyst. It is therefore not surprising that the influence of water on the reaction appears anomalous when contrasted with the cases dealt with in the present paper.

Experimental.

The apparatus employed for measuring the electromotive forces was that used during the experiments described in Part I. (this vol., p. 1420). The anhydrous alcohol and solutions of hydrogen chloride were prepared as on the former occasion.

The cells used were a pair, each of which was a simple modification of a type in common use, but were joined by means of a narrow glass U-tube. Each cell was provided with a raised reservoir of the solution and with suitable taps, by means of which the levels of the liquids in the cells could readily be adjusted or contact between the cell liquids secured.*

Readings were made by first opening three of the four taps separating the two cells; usually there was enough leakage through the fourth to allow of an approximate estimate of the potential, which could therefore be nearly balanced before this stopcock was opened to obtain a more exact reading. Even after many measurements had been made, involving opening all four taps, the potential varied but imperceptibly, and in no case where numbers are given without comment was there any evidence that a variation in potential had been caused by mixing of the solutions.

Before each experiment the cells and U-tube were carefully cleaned, washed with pure anhydrous alcohol, and dried at 100°.

* The more convenient method usually employed in working with the hydrogen electrode is to use one cell in combination with a calomel electrode; thus, Denham (Trans., 1908, **93**, 41) was able to obtain very satisfactory results with aqueous solutions of salts of weak bases, employing such a combination. In the case of alcoholic solutions of hydrogen chloride, however, the calomel electrode has not given such sharp results as the hydrogen electrode, so that it was thought desirable to avoid its use in the present series of measurements.

All measurements were made at $25° \pm 0·05$.

In preliminary experiments very unsatisfactory results were obtained, both with electrodes of platinum foil and with others made of platinum films deposited on glass; this was finally found to be due almost wholly to the condition of the platinum surfaces. Constant electromotive forces and consistent results were obtained with platinum plates only when these had been heated to redness, platinised in the usual manner, and washed repeatedly, first with water and then with absolute alcohol, and transferred at once, while still moist, to the cells. At the moment before the insertion of the electrodes the whole of the remainder of the apparatus should otherwise be in full working order, and a fairly rapid stream of hydrogen should have been passing for a sufficiently long time to ensure the complete expulsion of all other gases from the vessels, tubes, and solutions. The electrodes should not be used twice, but require cleaning with boiling nitric acid, replatinising, and treating as above before each new experiment.

Electrodes of platinised glass, if newly prepared, coated with platinum black, washed as above and used at once, also gave excellent results, identical with those obtained with the foil-electrodes, but as it was necessary after each experiment to renew the main films and they offered no advantages as compared with the other type of electrodes, their use was discontinued.

When the apparatus was working in a satisfactory manner it was observed that a nearly steady electromotive force was obtained in one or two minutes after the electrodes had been inserted, and when this was not the case, experience showed that it was useless to continue the experiment; if the cells were short-circuited with open taps for several seconds and the circuit then broken, the original potential was attained once more in less than a minute.

Results.

Measurements made during some typical experiments at 25° are given below. In each of the cases which follow immediately, the solutions used in the two cells were prepared from the same specimen of alcohol.

The time is given in hours after the observations were began, usually within two minutes of the insertion of the electrodes. The potentials given are the means of several readings in each case.

The arrows indicate the direction of the positive current inside the cells.

The observations in the two experiments which follow immediately are given to show the influence of time on the potentials observed.

They were chosen at random from a large number of similar records.

(1) *With Slightly Moist Alcohol as Solvent* (*Commercial Absolute*).

$$H_2,1{\cdot}114N\text{-HCl}\,|\,0{\cdot}1021N\text{-HCl},H_2.$$
$$\longleftarrow$$

Time.	Potential.	Time.	Potential.
0·0 hour	0·0447 volt	1·75 hours	0·0467 volt *
0·5 ,,	0·0447 ,,	2·5 ,,	0·0467 ,,
1·0 ,,	0·0467 ,,	3·25 ,,	0·0467 ,,

* Although the accuracy of the potentials is not guaranteed within much less than a millivolt, individual readings could be compared within 0·2—0·3 millivolt. For the sake of comparisons the calculated means are given in all cases to 0·1 millivolt.

[With cells reversible to chloridion and prepared with the same two solutions, the potential obtained was 0·060 volt at the same temperature.]

(2) *With Alcohol dried over Calcium.*

$$H_2,0{\cdot}6341N\text{-HCl}\,|\,0{\cdot}06408N\text{-HCl},H_2.$$
$$\longleftarrow$$

Time.	Potential.	Time.	Potential.
0·0 hour	0·0291 volt	1·5 hours	0·0283 volt
0·66 ,,	0·0283 ,,	4·0 ,,	0·0289 ,,
0·91 ,,	0·0283 ,,		

The slight rise indicated in the last reading was perhaps due to a slight mixing of the solutions during the considerable time occupied by the experiment.

A number of comparative experiments were made in the early part of the investigation with different electrodes. In all cases where the alcohol was moist a sensibly constant potential was reached within fifteen minutes; thus with solutions of hydrogen chloride in two different concentrations in the cells with 99·7 per cent. alcohol as solvent, tests with seven different electrodes gave potentials between 0·0424 and 0·0490 volt. On the other hand, with solutions prepared from calcium-dried alcohol, constant values of the potentials were obtained almost as soon as it was possible to begin making measurements; thus with 0·6341*N*-hydrogen chloride and 0·06408*N*-hydrogen chloride respectively in absolute alcohol, five different pairs of electrodes of platinised foil gave potentials identical with one another within the limits of the bridge-readings, namely, $0{\cdot}0282 \pm 0{\cdot}0003$ volt. This value is in close agreement with that required, namely, 0·02806 volt if the transport number $(1-n)$ of the chloridion in the solutions is taken as 0·32, which is nearly that deduced by other methods (compare this vol., p. 1420).

Other experiments were made with solutions of hydrogen chloride with concentrations considerably lower than the above; thus the arrangement:

$$\underset{\longleftarrow}{H_2,0{\cdot}100N\text{-}HCl\,|\,0{\cdot}010N\text{-}HCl,H_2}$$

gave a potential of 0·0214 volt, or some seven millivolts less than that obtained for the stronger solutions having much the same total concentration ratio. Other measurements with several different samples of alcohol have shown that when either cell contains a solution having a concentration of hydrogen chloride less than about $N/20$, the potential differences, although steady and reproducible with considerable accuracy, are invariably smaller than those calculated with the above formula by several millivolts. The explanation which first suggests itself, namely, that the value used for the transport number of chloridion in alcohol is too low, or variable, must, in the authors' opinion, be rejected; further, the presence of a constant small quantity of water or other impurity more basic than alcohol would have an influence in the opposite sense from that observed. Pending further investigation, this record of the general nature of these results is the only contribution which need be made at the present time.

The unexpected sharpness of the potentials and the accuracy with which they are reproduced led the authors to proceed at once to the main object they had in view, namely, to investigate the effect of water on the potential of the hydrogen electrode in alcohol, with the results recorded in the following section.

The Influence of Small Quantities of Water on the Potential of the Hydrogen Electrode in Alcoholic Hydrogen Chloride.

The experiments on this aspect of the subject were carried out in much the same manner as those above described. In most cases the contents of one of the cells were quite dry, whilst those of the other contained a known concentration of water.

In the experiments *c*, *d*, *e*, *f*, the total concentration of the hydrogen chloride in the two cells was the same, but varying quantities of water were present in one cell liquid only. The direction of the positive current in the cells was always from the moist solution to the anhydrous one.

In one column are given the values of P'/P calculated by means of the formula (5):

$$E=\frac{RT}{F}\log_e\frac{P}{P'}.$$

These represent the apparent relative values of the concentrations of the free hydrogen ions, or the apparent relative values of the

availability of the acid, in the moist as compared with the anhydrous solution. Cases *b* and *c* approach most nearly the ideal state of low concentration, *c* representing the most dilute solution of hydrogen chloride with which sharp readings could be taken, and *b* the case where still more dilute acid was used with a subsidiary electrolyte.

The values of r, the apparent "water-value" of alcohol at 25°, were calculated by means of the formula (Trans., 1910, **97**, 22):

$$P' = Pr/r + w,$$

where P' is the availability of the acid in the moist solution, P that of the acid in the anhydrous solution, and w represents the number of gram-molecules of water present in one litre of the moist solution.

The numbers given under (*b*) represent the means of three sets of results, concordant within two millivolts, obtained with three samples of $N/500$-hydrogen chloride in alcohol in presence of an equal concentration of purified lithium chloride ($N/10$) in both cells. Readings were sharp, and were easily made.

(*b*) 0·002*N*-HCl *and* 0·100*N*-LiCl *in both cells;* varying quantities of water in the second cell.

Potential.	w.	P'/P.	r.
0·0384 volt	0·444	0·224	0·128
0·0467 ,,	0·666	0·163	0·129
0·0590 ,,	1·00	0·108	0·122

In case (*c*) readings were also fairly sharp, but in absence of a subsidiary electrolyte measurements were very difficult with solutions less concentrated than $N/100$.

(*c*) 0·01*N*-HCl *in both cells;* water in one cell only.

Potential.	w.	P'/P.	r.
0·0420 volt	0·555	0·195	0·135
0·0551 ,,	1·00	0·117	0·132

(*d*) 0·020*N*-HCl *in both cells;* water in one cell only.

Potential.	w.	P'/P.	r.
0·0187 volt	0·222	0·48	0·205
0·0298 ,,	0·444	0·31	0·199
0·0400 ,,	0·666	0·20	0·166
0·0476 ,,	0·888	0·156	0·164
0·0515 ,,	1·00	0·134	0·155

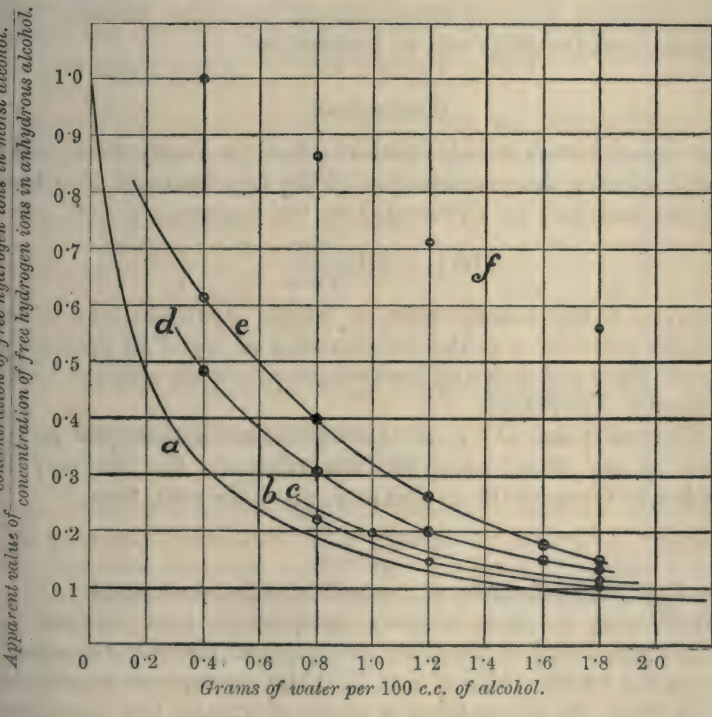
(*e*) 0·0853*N*-HCl *in both cells;* water in one cell only.

Potential.	*w*.	*P'/P*.	*r*.
0·0123 volt	0·222	0·62	0·363
0·0237 ,,	0·444	0·40	0·296
0·0347 ,,	0·666	0·26	0·234
0·0440 ,,	0·888	0·18	0·195
0·0484 ,,	1·00	0·152	0·179

(*f*) 0·8446*N*-HCl *in both cells;* water in one cell only.

Potential.	*w*.	*P'/P*.	*r*.
0·0000 volt	0·224	1·0	—
0·0040 ,,	0·444	0·86	2·74
0·0090 ,,	0·666	0·71	1·63
0·0140 ,,	1·00	0·57	1·33

In the diagram the results of the latter part of the investigation are expressed graphically, and the apparent values of P'/P, or the



relative concentrations of the free hydrogen ions, are indicated in the curves *b*—*f* corresponding with the experiments indicated with these letters.

The curve (*a*) is that deduced from measurements of the effect of water on the catalytic activity of very dilute hydrogen chloride

in alcohol, adopting 0·1 as the most probable value of r. The curve representing the results of Goldschmidt and Udby on esterification lies just above c, and its separate insertion on the diagram was hardly possible. Similarly, the results obtained from measurements of the salt-forming power of extremely dilute hydrogen chloride in alcohol is nearly coincident with a and slightly below it. Generally speaking, the more dilute the acid with which the experiments are made the lower the position of the curve on the diagram.

Attention may be drawn to the fact that any tendency for lithium chloride to withdraw part of the water from alcoholic solutions would have the result of raising b towards or above c, but a further result would be a decrease in the apparent value of r with increase in the concentration of water, and there is little evidence of this in the experiments made so far. The value of r in presence of lithium chloride requires determination by other methods, and experiments on the point will be undertaken.

Conclusions.

The solvate theory of acids indicates that, in highly dilute moist alcoholic solution the concentration of the free hydrogen ions from a mineral acid may be represented by the expression:

$$[H] = [H_0]\frac{r}{r+w}.$$

where $[H_0]$ is the concentration of "free" hydrogen ions in the anhydrous solution, w is the concentration of water in gram-molecules per litre, and r is the "water-value" of the alcohol at the temperature referred to.

If the conception of "free" hydrogen ions is discarded in the absence of any direct proof of their existence, the law may be expressed in terms of the availability, P, of the acid, thus:

$$P = P_0\frac{r}{r+w},$$

where P_0 is the availability of the acid in anhydrous solution.

Experiments on three entirely independent lines confirm the general applicability of the above formula, and the only discrepancy concerns the precise value of r at 25°; this discrepancy is probably due, however, to the small magnitude of r, and the consequent difficulties in fully eliminating all sources of experimental error, especially as with low concentrations of acid the solutions are very sensitive to certain impurities.

The following estimates of the value of r at 25° have now been made:

A. *By Measurements of Esterification Velocities* (Catalysis).
(i) $r=0{\cdot}15$ (Goldschmidt and Udby).
(ii) $r=0{\cdot}10$—$0{\cdot}11$ (Lapworth and Partington).
(iii) $r=0{\cdot}09$—$0{\cdot}095$ (Jones and Lapworth).

B. *By Measurements of Salt-forming Power* (Availability).
(iv) $r=0{\cdot}089$—$0{\cdot}108$ (Lapworth and Partington).
(v) $r=0{\cdot}095$ (Jones and Lapworth).

C. *By the* E.M.F. *of the Hydrogen Electrode* (Concentration of free $H^{\cdot}$ ions).
(vi) $r=0{\cdot}127$ (Hardman and Lapworth).

Having regard to the numerous sources of error, the numbers given in this communication are only quoted as being approximately correct, and many of the more important ones will be redetermined, with such additional precautions as may suggest themselves; the inquiry into electromotive forces and equilibria in alcohol and other organic media will be extended along lines similar to those suggested in this and previous papers.

Part of the expense of this investigation was defrayed by a grant from the Government Grant Research Fund of the Royal Society, for which the authors desire to express their indebtedness.

Schunck Laboratory,
University of Manchester.

CCL.—*Polymorphic Phthalylhydrazides.*

By Frederick Daniel Chattaway and Donald Frederick Sandys Wünsch.

Some years ago it was observed that hot saturated solutions of phthalylphenylhydrazide almost invariably deposited crystals of two distinct forms, one orange and the other of so pale a yellow as to seem almost colourless when viewed beside the orange modification; these crystals could easily be separated by hand, and each modification could be obtained in a pure state free from the other by allowing crystallisation to take place at a suitable temperature.

Dunlap (*J. Amer. Chem. Soc.*, 1905, **27**, 1091) published an account of similar observations while the work was in progress, and it was consequently discontinued.

The authors have recently resumed the subject to ascertain if this property of crystallising in two differently coloured forms is common to all the phthalylhydrazides.

So far, only one other instance has been found among the simple phthalyl derivatives, but it seems certain that this is due to the exact conditions necessary for the first appearance of the less highly coloured modification not having been realised in the remaining cases. Many observations on related compounds, which will be communicated later, lead to the conclusion that it should be possible to obtain every phthalyl- and substituted phthalylhydrazide in two modifications differing widely in colour and in crystalline form.

The phthalylhydrazides are very easily obtained by heating together at about 100° equivalent amounts of phthalic anhydride and the corresponding hydrazine, when water is eliminated, thus:

$$C_6H_4{<}{}^{CO}_{CO}{>}O + H_2N{\cdot}NHR = C_6H_4{<}{}^{CO}_{CO}{>}N{\cdot}NHR + H_2O.$$

The phthalylhydrazides crystallise extremely well from all ordinary solvents. The modifications separating at the higher temperatures are orange, whilst those separating at the lower temperatures are much paler, in fact, almost colourless. In every case where only one modification has been obtained it is the one having the deep orange colour.

Instances like the foregoing, in which organic substances of the same composition exist in forms showing distinctly different properties, are very frequent.

Such diversities in the case of liquids or gases can always be referred to differences in either the size or structure of individual molecules, and can therefore be formulated according to conventional usage by different structural formulæ. But among solids of the same composition the dissimilar properties may be due either to a difference in the size or the atomic arrangement of the individual molecules, that is, to polymerism or isomerism, or to a difference in the manner in which the molecules group themselves when the substance assumes the crystalline condition—that is to polymorphism. Although differences of atomic arrangement are generally associated with marked differences in chemical behaviour, whilst differences in molecular grouping only cause variations in the physical properties, it is not always easy to decide whether any given pair of substances are isomeric or polymorphic. They are usually regarded as isomeric if any differences of behaviour observed in the solid state persist when the compounds are dissolved, melted, or gasified, or if the two forms in specified reactions carried out under similar conditions yield different derivatives.

The two modifications of the phthalylhydrazides differ only in colour and crystalline shape, and the dissimilarity, so far as is known at present, disappears when the distinct solid substances are

dissolved. They must therefore provisionally be regarded as polymorphic, and not as isomeric or polymeric modifications. Since, however, the phthalylhydrazides may have the unsymmetrical configuration, the possibility that they may be stereoisomerides ought not to be lost sight of.

No differences in the chemical behaviour of the two forms have been observed; it should be noted, however, that their peculiar nature makes it impracticable to obtain derivatives which might decide the point beyond question.

The polymorphic phthalylhydrazides are enantiotropic, the two forms transforming at a definite temperature much below the melting point of either. The change in the solid state, however, takes place so slowly that it is possible for either form to exist in a more or less unstable condition at a temperature below or somewhat above the transition temperature for a limited period, depending on the rate of transformation. The transition points of the two pairs of polymorphic phthalylhydrazides described in this paper are at the present time being determined, and appear not to be very far removed from the ordinary temperature.

On heating a crystal of the colourless modification of phthalylphenylhydrazide to a temperature approaching 100°, the rate of transformation is so much increased that specks of the yellow modification almost at once appear, and grow into the mass until the whole is transformed. This conversion into the orange-coloured form takes place more easily when the white crystals are heated in a saturated alcoholic or acetic acid solution to about 60° or 70°.

Transformation of the orange-coloured phthalylphenylhydrazide into the colourless modification is so slow at the ordinary temperature that, not only may the yellow and colourless crystals be kept in contact for years without apparent change, but both forms can exist side by side for days in a saturated alcoholic solution without the orange-coloured crystals appreciably diminishing or the white crystals increasing in size.

Crystals of the pale yellow modification of phthalylphenylmethylhydrazide similarly transform quickly into the orange when heated to the neighbourhood of 100°, while the orange-coloured crystals when dry remain unchanged for months at the ordinary temperature. On the other hand, if crystals of the orange-coloured modification of phthalylphenylmethylhydrazide are placed in a saturated alcoholic solution at the ordinary temperature in presence of a crystal of the pale modification, they become completely transformed in a few hours, the orange-coloured crystals dissolving, and well-shaped crystals of the very pale yellow form taking their place.

Either form of phthalylphenylhydrazide or of phthalylphenyl-

methylhydrazide can be obtained at will by slightly supersaturating a solution above or below the transition temperature, and placing in it a crystal of the required modification. As, however, the difference in solubility of the two forms is at any temperature slight compared with the change of solubility as the temperature varies, a hot solution on cooling may pass into the metastable or even into the labile condition for the pale form, even when crystals of the orange form are present, so that, as might be expected, crystals of both modifications frequently separate together.

For convenience of reference the crystallographic constants of the substances described in this paper are given in the following table[1]:

Hydrazide.	Modification.	System.	Crystallographic constants.
Phthalylphenyl	Bright yellow	Monoclinic	$a:b:c=1{\cdot}1573:1:1{\cdot}2040$; $\beta=126°26'$
Phthalylphenyl	Pale yellow	Orthorhombic	$a:b:c=1{\cdot}0875:1:0{\cdot}5568$
Phthalyl-*p*-tolyl	Deep orange	Monoclinic	$a:b:c=1{\cdot}7525:1:0{\cdot}7914$; $\beta=126°30'$
Phthalyl-*o*-tolyl	Bright orange	Monoclinic	$a:b:c=0{\cdot}5555:1:0{\cdot}7491$; $\beta=96°5'$
Phthalyl-*p*-bromophenyl	Bright yellow	Monoclinic	$a:b:c=1{\cdot}5047:1:$? ; $\beta=103°7'$
Phthalyl-*p*-chlorophenyl	Bright yellow	?	?
Phthalylphenylmethyl	Bright orange	Triclinic	$a:b:c=0{\cdot}5853:1:0{\cdot}3801$; $\alpha=110°0'$, $\beta=114°16'$, $\gamma=68°17'$
Phthalylphenylmethyl	Pale yellow	Monoclinic	$a:b:c=0{\cdot}7569:1:0{\cdot}5306$; $\beta=92°10'$
Phthalylphenylbenzyl	Bright orange	Monoclinic	$a:b:c=0{\cdot}8873:1:0{\cdot}7729$; $\beta=93°49'$
Phthalyl-α-naphthyl	Orange	?	?
Phthalyl-β-naphthyl	Orange	?	?

Phthalylphenylhydrazide, $C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>N\cdot NH\cdot C_6H_5$.

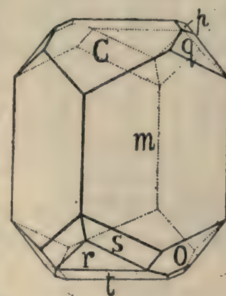
Phthalylphenylhydrazide has been described by Pickel (*Annalen*, 1886, **232**, 232), Hötte (*J. pr. Chem.*, 1886, [ii], **33**, 99; 1887, [ii], **35**, 265), Pellizzari (*Gazzetta*, 1886, **16**, 203), Just (*Ber.*, 1886, **19**, 1204), Henriques (*Ber.*, 1888, **21**, 1616), and Eibner and Merkle (*Ber.*, 1902, **35**, 2300). Their descriptions of the compound do not agree, especially as regards its colour, evidently owing to one or other of the modifications only having been observed. It is best obtained by dissolving phthalic anhydride in alcohol, adding the equivalent amount of phenylhydrazine, freshly distilled and free

[1] This and all the other descriptions of the crystals given in this paper have been furnished to us by Mr. T. V. Barker, Demonstrator of Mineralogy in the University of Oxford.

from aniline, evaporating off the alcohol, and heating the yellow, solid mass remaining on a water-bath until water-vapour ceases to be given off.[1]

The bright yellow form is best obtained by dissolving as much of the compound as possible in boiling glacial acetic acid or toluene, cooling slightly, and, after adding a few specially chosen crystals of this modification, allowing the temperature to fall very slowly. This operation is most conveniently carried out by placing the carefully corked flask in a hot water-jacketed cooler, so surrounded by cotton waste that several days are required for the temperature to fall to that of the laboratory. Bright yellow, monoclinic crystals of short and compact habit then separate, invariably free from crystals of the pale-coloured modification.

FIG. 1.



Phthalylphenylhydrazide (yellow modification).

The ratios of the axes are $a:b:c = 1·1573:1:1·2040$; $\beta = 126°26'$. The following forms were observed: $m-\{110\}$, $c-\{001\}$, $t-\{\bar{2}03\}$, $r-\{\bar{1}01\}$, $q-\{011\}$, $o-\{\bar{1}11\}$, $s-\{\bar{2}11\}$, $p-\{\bar{1}12\}$, and $e-\{012\}$. The habit of the crystals is shown in Fig. 1, the form e being rarely observed. Following is a table of measured and calculated angles:

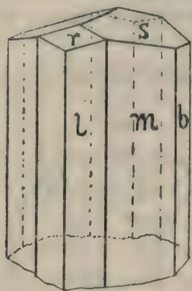
	No.	Limits.	Mean.	Calc.
$mm = 110 : 1\bar{1}0$	7	87°15′—87°33′	*87°20′	—
$mc = 110 : 001$	3	65 52 —65 59	65 56	65°51′
$mq = 110 : 011$	8	38 51 —39 10	*39 2	—
$cq = 001 : 011$	15	44 44 —44 52	*44 48	—
$ce = 001 : 012$	2	26 15 —26 20	26 17	26 24
$pt = \bar{1}12 : \bar{2}03$	3	32 50 —33 10	32 59	33 1
$mq = \bar{1}10 : 011$	12	78 40 —78 52	78 45	78 41
$ct = 001 : \bar{2}03$	2	43 11 —43 34	43 22	43 16
$tr = \bar{2}03 : \bar{1}01$	2	20 56 —21 2	20 59	21 6
$os = \bar{1}11 : \bar{2}11$	4	29 26 —29 42	29 34	29 22

There is a perfect cleavage parallel to $c-\{001\}$, an imperfect one parallel to $m-\{110\}$. The optical extinction on m is straight, and an optic axis emerges obliquely through q. D_4^{15} 1·356. Molecular volume = 175·5.

The pale yellow form is best obtained by saturating toluene with the compound at about 50°, boiling for a few moments to remove all traces of crystals from the sides of the flask, and allowing to

[1] If the mass is heated much above 100° or fused, the hydrazide partly or completely decomposes according to the duration of the heating into phthalanil, ammonia, and nitrogen.

FIG. 2.



Phthalylphenylhydrazide (pale modification).

cool to about 25°. As a rule, no crystals separate. A carefully chosen fragment of the pale yellow modification is then added, and the temperature slowly allowed to fall in the cooler to that of the laboratory. The pale yellow form then separates, free from crystals of the more highly coloured form, in very faintly tinted orthorhombic plates, with $a:b:c=1{\cdot}0875:1:0{\cdot}5568$. The observed forms were: $b-\{010\}$, $m-\{110\}$, $r-\{101\}$, $o-\{212\}$, $l-\{210\}$, $q-\{011\}$, $s-\{012\}$, and $n-\{230\}$. A typical crystal is shown in Fig. 2, and the observed and calculated angles follow:

		No.	Limits.	Mean.	Calc.
bn	= 010 : 230	2	31°27′—31°39′	31°33′	31°31′
bm	= 010 : 110	20	42 28 —42 46	*42 36	—
ml	= 110 : 210	3	18 42 —18 49	18 46	18 52
bo	= 010 : 212	1	—	76 7	76 5
bq	= 010 : 011	2	60 51 —60 53	60 52	60 53
bs	= 010 : 012	5	74 17 —74 28	74 23	74 26
mr	= 110 : 101	6	71 59 —72 6	*72 2	—
rq	= 101 : 011	4	38 53 —39 7	39 3	38 57

There is a fairly good cleavage parallel to $b-\{010\}$. Optically, the crystals clearly show their orthorhombic symmetry, the first mean line being parallel to the axis, a, with axial plane $c-\{001\}$; $2H_{Na}=ca\ 70°$, $\rho>v$. D_4^{17} 1·354. Molecular volume = 175·8.

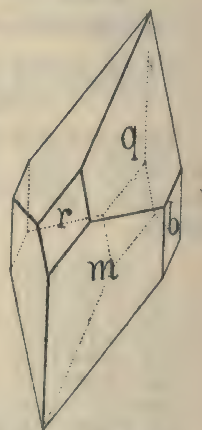
The pale yellow modification when placed in a saturated solution in any solvent at about 60° rapidly dissolves and disappears, whilst deep yellow crystals separate out, so that the pale compound appears to transform into a more highly coloured one. The crystals separating often preserve to some extent the plate-like shape of the pale yellow modification, but when examined with a lens are seen to be paramorphs, consisting of small crystals of the yellow form. Determinations of the solubilities which are proceeding indicate that the transition temperature is not far above the ordinary. Transformation also takes place when the pale crystals are heated alone, but more slowly than in presence of a solvent. If large crystals of the pale form are heated to 100°, deep yellow spots quickly appear, and extend through the crystals until, after some hours' heating, the latter are transformed into opaque paramorphs of the yellow modification. This transformation is much more rapid at a higher temperature, and prevents the melting point of the pale modification being determined; even with rapid heating transformation is complete before the melting point is reached. The deep yellow modification melts at 184°. So far the transforma-

tion of the yellow into the pale modification has only been effected by dissolving the former, and allowing the pale modification to crystallise out at a comparatively low temperature. The rate of transformation at the ordinary temperature is so slow that crystals of the two forms can be left for weeks in a saturated alcoholic solution without any appreciable growth of the pale crystals. In the solid state the yellow form can be left in contact with the pale form for years at the ordinary temperature without any perceptible alteration.

*Phthalyl-*p*-tolylhydrazide*, $C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}N\cdot NH\cdot C_6H_4Me$.

This substance is best prepared by dissolving equivalent amounts of phthalic anhydride and *p*-tolylhydrazine in alcohol, evaporating to dryness, and heating the solid residue on a water-bath until water-vapour is no longer given off. It is moderately readily soluble in boiling alcohol, toluene, or acetic acid, and separates in long, deep orange-yellow, prismatic crystals, which melt at 196°. The colour of this compound is very similar to that of the bright yellow modification of phthalylphenylhydrazide, but of a somewhat deeper shade. No pale modification corresponding with the second form of phthalylphenylhydrazide has yet been obtained. When crystallised from any solvent the orange modification separates, both at high and low temperatures:

FIG. 3.



*Phthalyl-*p*-tolylhydrazide.*

0·3092 gave 29·4 c.c. N_2 (moist) at 11° and 758 mm. N = 11·25.

$C_{15}H_{12}O_2N_2$ requires N = 11·11 per cent.

The crystals proved to be monoclinic with $a:b:c = 1{\cdot}7525:1:0{\cdot}7914$; $\beta = 126°30'$. The observed forms were: $m - \{110\}$, $q - \{011\}$, $b - \{010\}$, and $r - \{101\}$. The forms m and q predominated equally, whilst b was much smaller and r often failed. The habit is shown in **Fig. 3**.

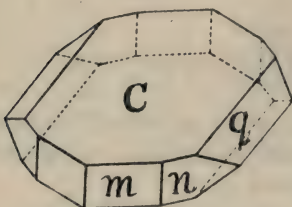
	No.	Limits.	Mean.	Calc.
bm = 010 : 110	2	35°25′—35°33′	35°29′	35°29
mm = 110 : $\bar{1}$10	4	70 36 —70 52	*70 44	—
mq = 110 : 011	7	43 12 —43 21	*43 16	—
mr = 110 : 101	3	62 10 —63 5	62 33	62 41
rq = 101 : 0$\bar{1}$1	3	35 16 —35 58	35 40	35 47
qm = 0$\bar{1}$1 : 110	9	98 19 —98 37	*98 28	—
qq = 011 : 0$\bar{1}$1	2	64 34 —64 52	64 43	64 55

There was no observable cleavage; optically the crystals are in full agreement with monoclinic symmetry; the extinction on the face *m* makes an angle of 29° with the edge *mm*. D_4^{18} **1·319.** Molecular volume = 191·2.

Phthalyl-o-tolylhydrazide.

Phthalyl-o-tolylhydrazide was obtained exactly as the para-compound by the interaction at 100° of equivalent quantities of phthalic anhydride and *o*-tolylhydrazine. It is moderately readily soluble in all ordinary organic solvents, and crystallises well from hot alcohol, toluene, or glacial acetic acid in small, tabular, monoclinic crystals of a bright orange colour (compare Fig. 4), which melt at 198°. The pale modification has not yet been obtained:

FIG. 4.



Phthalyl-o-tolylhydrazide.

0·2648 gave 24·98 c.c. N_2 (moist) at 14° and 760 mm. N = 11·04.
$C_{15}H_{12}O_2N_2$ requires N = 11·11 per cent.

The calculated ratios of the axes are: $a:b:c = 0·5555:1:0·7491$; $\beta = 96°5'$. The forms observed were: $c-\{001\}$, $m-\{110\}$, $n-\{120\}$, and $q-\{011\}$. The measured and calculated angles follow.

	No.	Limits.	Mean.	Calc.
$qq = 011 : 0\bar{1}1$	3	73°13′—73°28′	73°20′	73°22′
$cq = 001 : 011$	5	36 31 —36 45	*36 41	—
$mq = \bar{1}10 : 011$	2	77 31 —77 40	77 35	77 37
$mq = 110 : 011$	3	68 38 —68 47	*68 42	—
$cm = 001 : 110$	2	84 40 —84 45	84 42	84 40
$nm = 120 : 110$	4	18 47 —19 30	19 1	18 56
$mm = 110 : 1\bar{1}0$	5	57 48 —57 56	*57 50	—

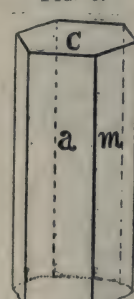
D_4^{13} 1·383. Molecular volume = 182·3.

Phthalyl-p-bromophenylhydrazide, $C_6H_4<^{CO}_{CO}>N\cdot NH\cdot C_6H_4Br$.

The interaction of phthalic anhydride and *p*-bromophenylhydrazine at 100°, under conditions similar to those previously described, produces *phthalyl-p-bromophenylhydrazide*. This compound is moderately readily soluble in all ordinary organic solvents, and crystallises from hot alcohol or toluene in bright yellow, monoclinic prisms, very closely resembling in colour the yellow modification of phthalylphenylhydrazide. It melts at 206°. The pale modification has not yet been obtained:

0·2022 gave 0·1226 AgBr. Br = 25·80.
$C_{14}H_9O_2N_2Br$ requires Br = 25·21 per cent.

FIG. 5.



Phthalyl-p-bromophenylhydrazide.

The crystals are six-sided prisms of the monoclinic system (compare Fig. 5), with the axial ratios having the values $a : b : c = 1\cdot5047 : 1 : \ ? \ ; \beta = 103°7'$. The only forms observed were $a-\{100\}$, $m-\{110\}$, and $c-\{001\}$, and the relative length of the vertical axis, c, could not accordingly be determined. The following angles were measured and calculated:

	No.	Limits.	Mean.	Calc.
$ma = 110 : 100$	5	55°34′—55°50′	55°41′	55°41′
$mm = \bar{1}\bar{1}0 : 1\bar{1}0$	6	68 35 —68 39	*68 37	—
$ca = 001 : 100$	3	76 49 —77 0	*76 53	—

There is no observable cleavage. D_4^{21} 1·682. Molecular volume = 188·5.

Phthalyl-p-*chlorophenylhydrazide*, $C_6H_4<\substack{CO\\CO}>N\cdot NH\cdot C_6H_4Cl$.

Phthalyl-p-*chlorophenylhydrazide* was prepared as above described from *p*-chlorophenylhydrazine. It resembles the *p*-bromo-compound very closely. It crystallises from hot alcohol or toluene in bright yellow prisms, which are too slender to admit of measurement. It melts at 191°:

0·1854 gave 0·1001 AgCl. Cl = 13·35.

$C_{14}H_9O_2N_2Cl$ requires Cl = 13·01 per cent.

Phthalylphenylmethylhydrazide, $C_6H_4<\substack{CO\\CO}>N\cdot NMePh$.

Phthalylphenylmethylhydrazide affords the best example of the dimorphism yet met with among compounds of this class, as each form can be easily obtained and transformed into the other. It is prepared exactly as the other hydrazides described in this paper by dissolving equivalent quantities of phthalic anhydride and phenylmethylhydrazine in alcohol, evaporating off the solvent, and heating the solid residue on a water-bath for some hours until water-vapour is no longer given off. The yield is practically theoretical. It is moderately soluble in all ordinary organic solvents, and crystallises well from hot solutions in toluene or alcohol. When such a solution is allowed to cool, the modification stable at the higher temperature crystallises out in long, bright orange-coloured, triclinic prisms. If these crystals are allowed to remain in the mother liquor for some days, stouter crystals of the modification stable at a lower temperature and exhibiting a very pale yellow tinge make their appearance, and grow at the expense of the orange-coloured crystals, which become etched, dissolve away, and finally disappear. At the ordinary temperature of the laboratory a few grams become completely transformed in a day or so, depending on the size of the

original crystals. The pale yellow crystals of the modification stable at the lower temperature being produced thus under ideal conditions, as the solution is always slightly supersaturated with regard to them, are especially fine in shape and appearance. When crystals of the pale form are placed in a saturated alcoholic solution at about 40°, they rapidly pass into solution, and crystals of the orange-coloured modification appear in their place. The exact transition point is being determined. When a crystal of the pale form is heated at 100°, specks of the yellow form soon appear, and grow until an opaque paramorph of the original crystal is produced, consisting of small crystals of the orange modification. This change becomes very rapid a few degrees above 100°, this being much below the melting point of the pale yellow modification, which consequently cannot be determined. The orange-coloured modification melts at 127°:

Orange Modification:—

0·3543 gave 34·2 c.c. N_2 (moist) at 15° and 758 mm. N=11·22.

Pale Yellow Modification:—

0·2333 gave 22·5 c.c. N_2 (moist) at 15° and 758 mm. N=11·21.

$C_{15}H_{12}O_2N_2$ requires N=11·11 per cent.

The essential difference between the two forms is clearly brought out by the following crystallographic determination, for they crystallise in different systems.

(1) *Orange Modification.*

The crystals are triclinic, and have the following crystallographic constants: $a : b : c = 0·5853 : 1 : 0·3801$; $\alpha = 110°0'$, $\beta = 114°16'$, $\gamma = 68°17'$.

Forms: $b-\{010\}$, $a-\{100\}$, $m-\{1\bar{1}0\}$, $c-\{001\}$, $r-\{101\}$, $p-\{\bar{1}01\}$, $q-\{0\bar{1}1\}$, and $o-\{\bar{1}\bar{1}1\}$. Two crops of crystals, from alcohol and toluene respectively, were found not to exhibit quite the same combination of forms; the crystals of the first crop showed all the forms enumerated with the exception of *r*, while those of the second crop were characterised by a combination of forms *b*, *a*, *m*, *p*, *c*, and *r*, and, moreover, were generally twins, with *b* as twin and composition plane. Typical crystals are shown in Figs. 6 and 7. The crystals were measured on the two-circle goniometer, and the observed and calculated values for the angles ϕ and ρ are given in the following table:

FIG. 6.

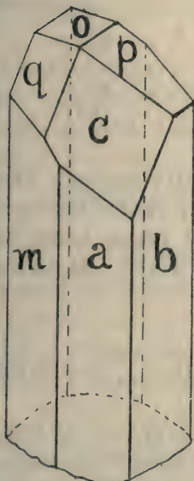
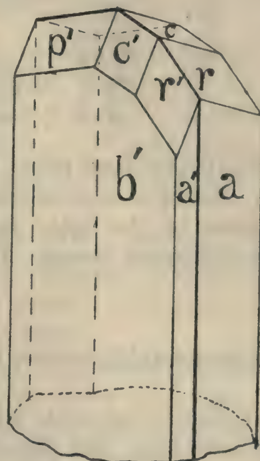


FIG. 7.



Phthalylphenylmethylhydrazide.
(*Single crystal.*) *Yellow modification* (*triclinic twin*).

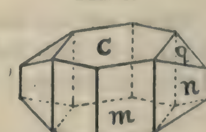
Form.	No.	Mean observed. ϕ.	ρ.	Calculated. ϕ.	ρ.
b-(010)	8	0° 0′	90° 0′	—	—
a-(100)	8	*105 32	90 0	—	—
m-(1$\bar{1}$0)	7	*130 56	90 0	—	—
p-($\bar{1}$01)	4	*329 53	*27 31	—	—
c-(001)	3	60 53	*27 20	60°44′	—
r-(101)	1	87 1	49 5	87 19	49°21′
o-($\bar{1}\bar{1}$1)	2	277 27	14 34	276 46	14 50
q-(0$\bar{1}$1)	2	109 54	25 45	110 22	25 41
a-(twin)	1	254 30	90 0	254 28	90 0
p-(twin)	1	210 15	27 38	210 7	27 31
c-(twin)	1	119 8	27 17	119 15	27 20
r-(twin)	1	92 36	49 0	92 41	49 21

Cleavage: perfect parallel to $b-\{010\}$, imperfect parallel to $m-\{1\bar{1}0\}$. D_4^{21} 1·352. Molecular volume = 186·5.

(2) *Pale Modification.*

A typical crystal is shown in Fig. 8. The crystals are monoclinic with $a:b:c=$ 0·7659 : 1 : 0·5306; $\beta = 92°10'$. Forms: $c-\{001\}$, $m-\{110\}$, $n-\{120\}$, $q-\{011\}$, and $o-\{111\}$; the last form was only observed once. The measured and calculated angles from three crystals are given in the following table:

FIG. 8.



Phthalylphenylmethylhydrazide (pale modification).

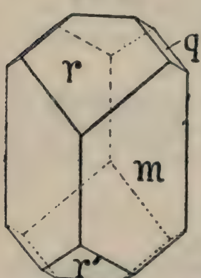
Face.	No.	Mean measured. ϕ.	ρ.	Calculated. ϕ.	ρ.
n-120	11	33°15′	—	33° 9′	—
m-110	11	*52 34	—	—	—
c-001	3	91 21	*2°10′	90 0	—
q-011	6	4 9	*28 1	4 17	—
o-111	1	54 9	42°15′	54 3	42°5′

Cleavage: parallel to basal plane {001} perfect. Optics: extinction on m 21°. An optic axis obliquely visible through {001}, and its position points to the optic axial plane being the plane of symmetry. Birefringence strong. D_4^{16} 1·327. Molecular volume = 189·9.

Phthalylphenylbenzylhydrazide, $C_6H_4<{CO \atop CO}>N\cdot NPh\cdot CH_2Ph$.

Phthalylphenylbenzylhydrazide was prepared as before described from phthalic anhydride and phenyl benzylhydrazine. It crystallises from alcohol or toluene in bright orange-coloured, monoclinic prisms (compare Fig. 9), which melt at 132°. The pale-coloured modification has not yet been obtained:

FIG. 9.



Phthalylphenylbenzylhydrazide.

0·2656 gave 20·2 c.c. N_2 (moist) at 18° and 756 mm. N = 8·69.

$C_{21}H_{16}O_2N_2$ requires N = 8·54 per cent.

The calculated ratios of the axes are: $a:b:c = 0·8873:1:0·7729$; $\beta = 93°49'$, the observed forms being: m – {110}, r – {101}, r' – {$\bar{1}$01}, and q – {011}. The predominant terminal face was always r – {101}; the form q – {011} was not present on all the crystals, and was very small.

Face.	No.	Limits. ϕ.	Limits. ρ.	Mean. ϕ.	ρ.	Calculated. ϕ.	ρ.
m-110	9	48°25′—48°34′	—	*48°29′	90° 0′	—	—
r-101	3	89 36′—90 17	43° 6′—43°23′	89 54	*43 13	90° 0′	—
r'-$\bar{1}$01	3	89 46 —90 0	38 46 —38 59	89 53	*38 53	90° 0	—
q-011	2	4 31 — 4 43	37 43 —38 1	4 37	37 52	4 52	37°48′

There was no observable cleavage; the optical extinction on the prism is 4° with the prism edge, on r – {101} diagonal. D_4^{17} 1·240. Molecular volume = 264·5. The double refraction is strong.

Phthalyl-α-naphthylhydrazide, $C_6H_4<\substack{CO \\ CO}>N\cdot NH\cdot C_{10}H_7$.

Phthalyl-α-naphthylhydrazide, which was prepared in the ordinary manner from α-naphthylhydrazine, crystallises from alcohol in slender, orange-coloured, flattened prisms, which melt at 221°:

0·3944 gave 31·7 c.c. N_2 (moist) at 10° and 760 mm. N = 9·58.

$C_{18}H_{12}O_2N_2$ requires N = 9·7 per cent.

Phthalyl-β-naphthylhydrazide,

Phthalyl-β-naphthylhydrazide, prepared as before from β-naphthylhydrazine, crystallises from alcohol in slender, orange-coloured, flattened prisms, which melt at 184°:

0·2673 gave 21·7 c.c. N_2 (moist) at 10° and 760 mm. N = 9·67.

$C_{18}H_{12}O_2N_2$ requires N = 9·7 per cent.

Both phthalyl-α-naphthylhydrazide and phthalyl-β-naphthylhydrazide crystallise well from hot alcohol or toluene, in which they are sparingly soluble, but neither compound gave crystals adapted for measurement. Only the orange-coloured modification of each was obtained.

The authors desire to thank Mr. T. V. Barker for his kindness in measuring and examining all the crystals described, and for much help during the progress of the work, and also the Government Grant Committee of the Royal Society for a grant which has partly covered the cost of the material used.

UNIVERSITY CHEMICAL LABORATORY,
OXFORD.

CCLI.—*The Influence of Inactive Electrolytes on the Optical Activity of* l-*Malic Acid in Aqueous Solution.*

By CLIFFORD MORGAN STUBBS (1851 Exhibition Scholar of the University of New Zealand).

ALTHOUGH the influence of solvents on the rotatory power of optically active solutes has been much studied in recent years, much more work remains to be done before its nature will be made generally clear. A field not yet very widely explored is the case of the addition of electrolytes to aqueous solutions of active

substances. A study of the effect of this change of solvent on the rotation might be fruitful in helping to a solution of the general problem. Apart from cases where chemical reaction between solute and added electrolyte takes place (for example, in the formation of well known active hydroxy-acid complexes), the influence of inorganic salts has been investigated in the case of certain active sugars by several workers, for example, Farnsteiner (*Ber.*, 1890, **23**, 3570), Rimbach (*Zeitsch. physikal. Chem.*, 1892, **9**, 707), Rimbach and Weber (*ibid.*, 1905, **51**, 473), and Wender (*Biochem. Zeitsch.*, 1911, **30**, 357). The effects generally are small, increase with increasing salt addition, and in some cases show regularities according to the periodic system. In the present research it was attempted to make a systematic and exhaustive study of the influence of electrolytes on the rotation of *l*-malic acid. The great sensitiveness of the latter to various solution changes, for example its formation of abnormally active complexes with salts of certain multivalent elements, and the actual change from lævo- to dextro-rotation during concentration of its aqueous solution (Schneider, *Annalen*, 1881, **207**, 257), together with the large number of data which this sensitiveness has called forth, make malic acid eminently suitable for the investigation.

There is one very obvious objection to its use, however, which must here be met, namely, the fact that it is itself an electrolyte, although a weak one, and that adjustment of ionic equilibrium will therefore complicate the observed effects. That this complicating influence is, however, very small is shown by the following calculation. In a typical case, to be described later, 0·25 of an equivalent of potassium chloride was added to 500 grams of a 20 per cent. solution of malic acid. The system would come to equilibrium according to the equation:

$$\begin{array}{ccccccc} H\bar{A} & + & KCl & \rightleftarrows & K\bar{A} & + & HCl \\ \alpha_1 & & \alpha_2 & & \alpha_3 & & \alpha_4 \\ 1-x & & n-x & & x & & x \end{array}$$

($\bar{A}$ represents the group $H_5C_4O_5$. The middle row gives the degree of dissociation, and the bottom row the gram-molecules present per V litres, of the various substances, when equilibrium is reached.) Then by a calculation due to Arrhenius and van Laar (compare also *Zeitsch. physikal. Chem.*, 1896, **19**, 485) the following equations are obtained:

$$\alpha_1\{(1-x)\alpha_1+(n-x)\alpha_2+x\alpha_3+x\alpha_4\}=kV(1-\alpha_1) \quad . \quad . \quad \text{(i)}$$

(k being the dissociation constant of $H\bar{A}$),

and $$(1-x)(n-x)\alpha_1\alpha_2=x^2\alpha_3\alpha_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

also, to a first approximation, $x^2=\dfrac{kV}{\alpha_3\alpha_4}$ . . . . (iii)

In the case under consideration, α_2, α_3, α_4 may be taken approximately equal, say, each to 0·78, the degree of dissociation of potassium chloride at the dilution used. It may be calculated that $V=0{\cdot}637$, and $n=0{\cdot}335$; also $k=3{\cdot}95\times10^{-4}$ (Ostwald, *Zeitsch. physikal. Chem.*, 1889, **3**, 369); hence from (iii), to a first approximation, $x=0{\cdot}0203$.

Therefore from (i), $\alpha_1=0{\cdot}00092$, and therefore from (ii) to a second approximation, $x=0{\cdot}01912$. Hence the percentage of potassium as hydrogen malate $=\dfrac{0{\cdot}01912\times100}{0{\cdot}335}=5{\cdot}706$; or percentage as undissociated hydrogen malate $=5{\cdot}706\times0{\cdot}22=1{\cdot}255$. The extent of ionic reaction is therefore in this and similar cases very small; and in actual practice any possible effect on the rotation due to it was completely overshadowed by large influences of another sort.

Experimental.

Apparatus and Method.—The rotation of the solutions was read by a Schmidt and Haensch three-field polarimeter; ten to fifteen readings being taken for each solution, in most cases an accuracy to within a few thousandths of a degree being attained. The temperature was in all cases 20°, the thermometer being standardised, and reading to tenths. Yellow sodium light was used, obtained from a flame illuminated by sodium chloride, and filtered through 2·5 cm. of a 6 per cent. solution of potassium dichromate, this giving (Landolt, "Das opt. Drehungsvermögen," p. 364) a mean wavelength of $589\mu\mu$. Density was determined by means of a pyknometer of about 15 c.c. content.

Kahlbaum's malic acid was used. Of the salts, most were the "pure, for analysis" salts used in the laboratory; a few had to be specially prepared; some (for example, zinc chloride) were obtained in solution, the strength of the latter being determined by analysis. For comparative purposes it was considered best to add the various salts in equivalent quantities to malic acid solutions of the same strength, namely, 100 grams of malic acid: 400 grams of water, in most cases. Such a solution is about 1·5 molecular, and, without being too concentrated, made possible sufficiently large and accurate results. Where the anhydrous electrolytes could not conveniently be used, hydrates or solutions of them were added to more concentrated malic acid solutions in such proportions that the ratio, malic acid : total water : equivalents of electrolyte, was as given. To make up the 20 per cent. solution above described, malic acid, dried over sulphuric acid until no further loss of weight occurred, was added to four times its weight of water. The composition determined by titration against barium hydroxide standardised by

succinic acid agreed satisfactorily with that by direct weighing. For five different 20 per cent. solutions prepared in the manner described from different samples of malic acid, the densities were:

$$d_4^{20} = (a)\ 1{\cdot}0793,\ (b)\ 1{\cdot}0797,\ (c),\ (d),\ \text{and}\ (e)\ 1{\cdot}0795.$$

The mean density was thus 1·0795. Other densities determined were:

for 5 per cent. solution $d_4^{20} = 1{\cdot}0180$
,, 40 ,, ,, $d_4^{20} = 1{\cdot}1713$.

On exhibiting these data graphically, the points lie on a regular curve passing through the point for which percentage=0, and density=1. If strengths and densities, as given by Schneider (*loc. cit.*), Nasini and Gennari (*Zeitsch. physikal. Chem.*, 1896, **19**, 117), Woringer (*ibid.*, 1901, **36**, 336), and Winther (*ibid.*, 1902, **41**, 161), are similarly represented by curves, it is seen that considerable divergencies exist between the several results, the author's curve being the middle one of the five. Concentration calculated from a given density would be about 5 per cent. lower according to Schneider and Woringer than according to the author or Nasini and Gennari. Recognising these differences, Woringer ascribed them to error on Nasini and Gennari's part. Both the latter and he determined concentration by titration against potassium hydroxide. The author believes that his gravimetric preparation of the solutions yields consistent (compare constancy of density of independently prepared 20 per cent. solutions, shown above) and trustworthy results, whilst according to Degener (*Festsch. d. Techn. Hochschule, Braunschweig*, 1897, p. 451) doubt attaches to the accuracy of a titration of malic acid against alkali. If the author be right, and Woringer in error, the latter's data will evidently need revision; and the same holds regarding Thomsen's results (*Ber.*, 1882, **15**, 441), where the composition of malic acid solutions is determined from density by a formula based on Schneider's data.

Rotation of Pure Malic Acid Solutions (l=2 dcm.).

TABLE I.

p.	α_D^{20}.	d_4^{20}.	$[\alpha]_D^{20}$.
5	−0·229°	1·018	−2·25°
20 (*a*)	−0·38	1·0793	−0·88
20 (*b*)	−0·42	1·0797	−0·97
20 (*c*)	−0·415	1·0795	−0·96
20 (*d*)	−0·41	1·0795	−0·95
20 (*e*)	−0·469	1·0795	−1·09
40	+0·500	1·1713	+0·535

The five different 20 per cent. solutions, for which data are tabulated above, were prepared from different samples of Kahl-

baum's malic acid. A repetition of the measurements in the cases (*a*) and (*e*), where the rotation varies most from the mean, confirmed the values given. The constancy of the density in the five cases shows that there was no appreciable difference in the percentage composition of the solutions; hence it must be concluded that the figures in the last column indicate actual differences in the rotatory power of the malic acid used. The explanation is no doubt to be found in the difficulty of obtaining chemically pure a substance so liable to the influence of traces of impurities, to polymerisation, anhydride-formation, and possibly racemisation.

In the following tables n=number of equivalents of salt added to 500 grams of a 20 per cent. solution of malic acid. Under the

Effect of Alkali Salts on the Rotation.

TABLE II.

Salt.	n.	d^{20}_{4}.	α^{20}_{D}.	$[\alpha]^{20}_{D}$.	$[\alpha]^{20}_{D}$ for pure acid.	Δ.
CsCl	$\frac{1}{4}$	1·1442	0·363°	0·86°	−1·08°	1·94°
CsCl	1	1·3185	1·413	3·58	−1·08	4·66
RbCl	$\frac{1}{4}$	1·1223	0·369	0·87	−1·08	1·95
RbCl	1	1·2417	1·598	4·00	−1·08	5·08
KCl	$\frac{1}{8}$	1·0905	0·07	0·16	−0·88	1·04
KCl	$\frac{1}{4}$	1·1013	0·455	1·07	−0·88	1·95
KCl	$\frac{1}{2}$	1·123	1·09	2·61	−0·88	3·49
KCl	1	1·1618	1·895	4·69	−0·88	5·57
KNO_3	$\frac{1}{4}$	1·1095	0·388	0·92	−0·96	1·88
KNO_3	1	1·1882	1·404	3·55	−0·96	4·51
KBr	$\frac{1}{4}$	1·1215	0·49	1·16	−0·95	2·11
KBr	1	1·2363	2·015	5·05	−0·95	6·00
(*a*) KI	$\frac{1}{4}$	1·1397	0·608	1·44	−0·95	2·39
KI	1	1·3015	2·283	5·84	−0·95	6·79
(*b*) K_2SO_4	$\frac{1}{4}$	1·1126	0·222	0·52	−0·96	1·48
NaCl	$\frac{1}{4}$	1·0993	0·30	0·70	−0·97	1·67
NaCl	1	1·153	1·86	4·51	−0·88	5·39
$NaNO_3$	$\frac{1}{4}$	1·107	0·275	0·65	−0·96	1·61
$NaNO_3$	1	1·180	1·482	3·68	−0·96	4·64
Na_2SO_4	$\frac{1}{4}$	1·1103	0·082	0·19	−0·95	1·14
Na_2SO_4	$\frac{7}{8}$	1·181	1·021	2·43	−0·95	3·38
NH_4Cl	$\frac{1}{4}$	1·086	0·08	0·19	−0·97	1·16
NH_4Cl	1	1·103	0·92	2·31	−0·97	3·28
NH_4NO_3	$\frac{1}{4}$	1·0938	0·064	0·15	−0·96	1·11
NH_4NO_3	1	1·131	0·794	2·04	−0·96	3·00
$(NH_4)_2SO_4$ ...	$\frac{1}{4}$	1·0965	−0·126	−0·30	−0·95	0·65
$(NH_4)_2SO_4$ ...	1	1·1418	0·416	1·03	−0·95	1·98
LiCl	$\frac{1}{4}$	1·091	−0·105	−0·24	−0·97	0·73
LiCl	1	1·123	0·775	1·87	−0·97	2·84

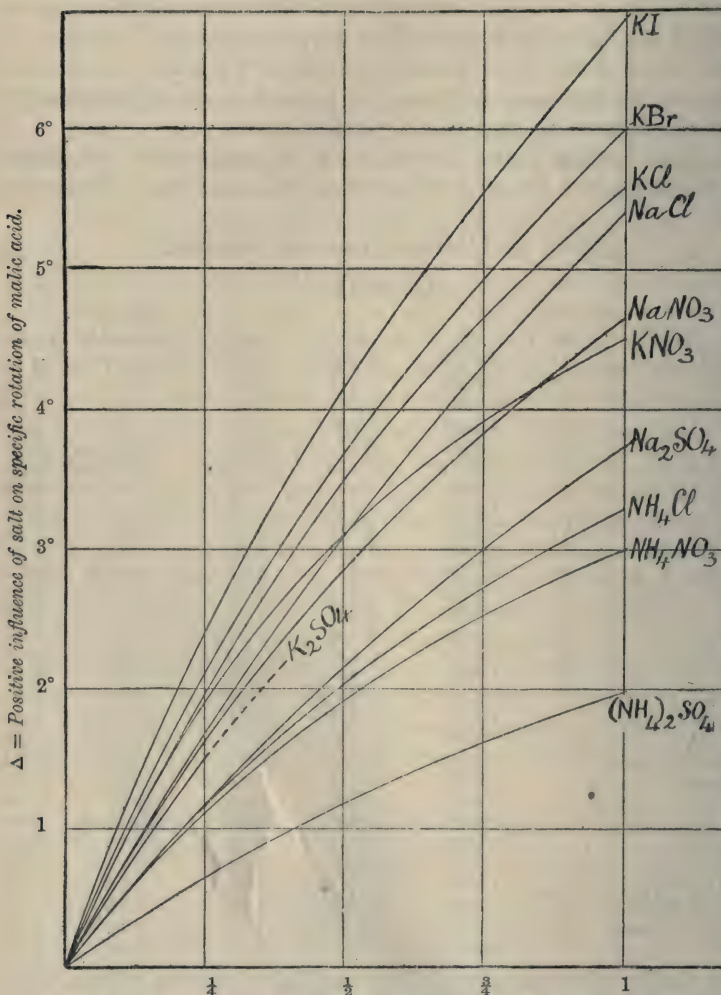
(*a*) Oxidation of the potassium iodide took place in the acid solution, which gradually turned brown; but when the readings were taken this action had probably not advanced far enough to affect them materially.

A projected measurement of the effect of potassium fluoride had to be abandoned, as sufficient hydrogen fluoride was liberated in the acid solution to have attacked and spoiled the glass polarimeter tube.

(*b*) Insufficient solubility prevented the use of a higher concentration of potassium sulphate.

column headed "$[\alpha]_D^{20}$ for pure acid" is given the specific rotation of the particular 20 per cent. solution of malic acid to which the salt was added. Δ denotes the change in a dextro-direction of the

FIG. 1.



n = number of equivalents of salt per 100 *grams of anhydrous malic acid.*

rotation caused by the addition of the salt, and is thus a measure of its influence on the rotation.

It is seen from the above table that in all cases the addition of the salts has markedly influenced the rotation, turning it in a

dextro-direction, and in most cases actually changing a lævo- into a dextro-rotation. If the typical case of potassium chloride is considered, it is seen how this influence, measured by Δ, varies continuously with the amount of salt added, Δ increasing as the amount of salt increases, but not quite proportionally. Fig. 1 shows graphically the influence of most of the alkali salts, Δ being plotted as ordinate, and the content in salt, n, as abscissa. There is thus obtained, for example, for potassium chloride, a very regular curve, passing through the origin and the four points determined, and with slight curvature convex upwards. For the other salts the data give only two points on each curve, besides the origin; but their position leaves no doubt that they lie on curves similar in point of regularity and of general appearance to that of potassium chloride. It was thought unnecessary to determine more points on these curves, those given illustrating with sufficient accuracy the nature of the result obtained.

The relative influences of the various salts are somewhat different at different concentrations; this is shown clearly in Fig. 1 by the varying curvature, and even crossing, of the curves. In investigating the connexion between the chemical nature of the salts and their comparative effects on the rotation, a definite equivalent concentration at which to compare these must therefore be chosen. An infinitely small concentration commends itself for this, for disturbing factors such as varying degree of dissociation of the salt, internal pressure, etc., will then be least evident; whilst at higher concentrations they may produce the divergencies from proportionality shown in the curves. Practical measurements of Δ being, however, impossible with a very small concentration of salt, an approximation will be obtained in comparing the values of Δ at the relatively low concentration for which $n=\frac{1}{4}$. Carrying out this comparison, it is evident from the curves that the influence of the salts on the rotation varies regularly with their chemical nature. For positive radicles the effects are in the order:

$$^{*}Cs>Rb>K>Na>NH_4>Li;$$

for negative, $I>Br>Cl>NO_3>\frac{1}{2}SO_4$. A numerical comparison reveals a striking regularity, shown by the following table:

TABLE III.

	Δ.	Diff.		Δ.	Diff.		Δ.	Diff.
KCl	1·95		KNO_3	1·88		$\frac{1}{2}K_2SO_4$ ...	1·48	
		0·28			0·27			0·34
NaCl	1·67		$NaNO_3$ ...	1·61		$\frac{1}{2}Na_2SO_4$ ...	1·14	
		0·51			0·50			0·49
NH_4Cl......	1·16		NH_4NO_3 ...	1·11		$\frac{1}{2}(NH_4)_2SO_4$	0·65	

* For "$n=\frac{1}{4}$" additions of salt the effects of cæsium, rubidium, and potassium chlorides are actually equal, but the shape of the curves (Fig. 2) seems to show that at lower concentrations of salt the order of influence is as given.

From the close agreement between the columns headed "Diff." it must be concluded that the effect of each of these alkali salts may be regarded as the sum of two terms, distinctive of the positive and negative radicles of the salt. The absolute value of the influence due to each radicle obviously cannot be decided, only the relative; for example, from the above table:

$$K - Na = \text{about } 0{\cdot}30^\circ.$$
$$Na - NH_4 = \text{about } 0{\cdot}50^\circ.$$

and consequently, $K - NH_4 = \text{about } 0{\cdot}80^\circ.$

From a consideration of the above results and those to be described, it seems probable that the main influence is exerted by the positive radicle.

Effect of Barium and Calcium Salts.

TABLE IV.

Salt.	n.	d_4^{20}.	α_D^{20}.	$[\alpha]_D^{20}$.	$[\alpha]_D^{20}$ for pure acid	Δ.
$BaCl_2$	¼	1·1256	1·976°	4·62°	−0·96°	5·58°
$BaCl_2$	1	1·2566	6·769	16·27	−0·96	17·23
(*a*) $Ba(NO_3)_2$	¼	1·133	1·652	3·88	−0·95	4·83
$CaCl_2$	¼	1·1018	1·226	2·86	−1·09	3·95
(*b*) $CaCl_2$	1·019	1·166	5·758	13·72	−1·09	14·81
(*b*) $Ca(NO_3)_2$	0·2998	1·1155	1·455	3·42	−0·95	4·37
$Ca(NO_3)_2$	1	1·1917	4·552	11·12	−0·95	12·07

(*a*) Insufficient solubility prevented the use of a higher concentration of barium nitrate.

(*b*) In these cases a too great quantity of salt was inadvertently added, as is shown under column "*n*." In the case of calcium nitrate, where the effect for $n = \frac{1}{4}$ is of interest for comparative purposes, interpolation gives 3·69° as the value of Δ for that concentration of salt.

The order of influence of the radicles of the above table is Ba>Ca, and as in the case of the alkali salts, $Cl > NO_3$. For the concentration $n = \frac{1}{4}$ we have:

TABLE V.

	Δ.	Diff.		Δ.	Diff.
$BaCl_2$	5·58°	1·63°	$Ba(NO_3)_2$	4·83°	1·14°
$CaCl_2$	3·95		$Ca(NO_3)_2$	3·69	

The numbers under "Diff." do not agree so closely as in the case of the alkali salts, barium nitrate giving a smaller effect than would be expected. It is very significant that, as appears from conductivity tables (Landolt-Börnstein, "Tabellen," p. 745), the dissociation of barium nitrate in aqueous solution at the concentration used is abnormally low; for whilst barium and calcium chlorides show practically equal degrees of dissociation in $N/2$-solution, that of barium nitrate is only about five-sixths that of calcium nitrate. A

connexion thus appears to exist between the degree of dissociation of a salt and its influence on the rotation of malic acid.

The most remarkable fact shown by table IV is the great influence exerted by salts of barium and calcium, especially when it is remembered that in equal equivalent concentrations there is only half an atom of these elements present to one atom of the alkalis. In order to determine whether this influence was connected with the valency of the metallic radicle, as well as to further the investigation generally, the effect of salts of other bivalent metals, and of the tervalent metal, aluminium, was measured.

Effect of Salts of Weaker Bases.

TABLE VI.

Salt.	n.	d_4^{20}.	α_D^{20}.	$[\alpha]_D^{20}$.	$[\alpha]_D^{20}$ for pure acid.	Δ.
$HgCl_2$	⅛	1·126	−0·257°	−0·60°	−0·96°	0·36°
$Hg(NO_3)_2$	¼	1·1495	−1·893	−4·45	−1·09	−3·36
$Hg(NO_3)_2$	1	1·3472	−1·900	−4·67	−1·09	−3·58
$Cd(NO_3)_2$	¼	1·1291	−0·150	−0·35	−1·08	0·73
$Cd(NO_3)_2$	1	1·267	0·831	2·03	−1·08	3·11
$ZnCl_2$	¼	1·1105	−0·226	−0·53	−1·09	0·56
$ZnCl_2$	1·015	1·1915	0·613	1·46	−1·09	2·55
$Zn(NO_3)_2$	¼	1·119	−0·229	−0·54	−1·09	0·55
$Zn(NO_3)_2$	1	1·2283	0·711	1·72	−1·09	2·81
$ZnSO_4$	¼	1·118	−0·406	−0·95	−0·95	0·00
$ZnSO_4$	0·998	1·2247	0·045	0·11	−0·95	1·06
$MgCl_2$	¼	1·0995	−0·137	−0·32	−1·09	0·77
$MgCl_2$	1	1·1556	0·729	1·73	−1·09	2·82
$Mg(NO_3)_2$	¼	1·107	−0·061	−0·14	−0·95	0·81
$Mg(NO_3)_2$	1	1·1817	0·699	1·70	−0·95	2·65
$MgSO_4$	¼	1·1095	−0·262	−0·61	−0·95	0·34
$MgSO_4$	1	1·1935	0·240	0·56	−0·95	1·51
$AlCl_3$	¼	1·0985	−0·209	−0·49	−1·09	0·60
$AlCl_3$	1	1·1547	0·655	1·54	−1·09	2·63
$Al_2(SO_4)_3$	¼	1·1075	−0·295	−0·69	−1·09	0·40

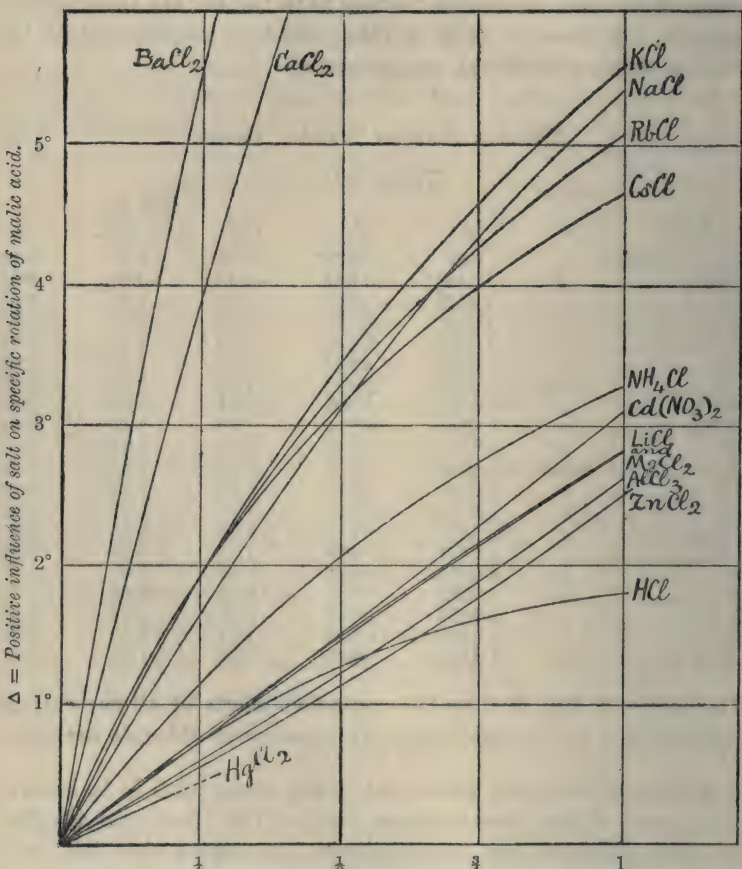
The curves in Fig. 2 show the respective effects of all the various chlorides used; also of cadmium nitrate, cadmium chloride not being used.

The effects of the salts mentioned in the above table is in general positive, and of the same order as that of the alkali and alkaline earth salts, although less in magnitude. It follows that the large influence of barium and calcium salts is not merely dependent on the valency of the metal. As was found in previous cases, so in table VI it is seen that the chloride and nitrate of any particular metal (with a notable exception, to which reference will be made later, in the case of mercury) exert about the same influence on the rotation, and the sulphate considerably less than either. The general effect of the metal radicles is in the order

$$Cd > Mg > Al > Zn > Hg.$$

More complicated relationships have, however, replaced the simple ones met with in the case of the alkali salts; so that to draw with any accuracy the curves representing the effects, more points than two or three would usually need to be determined. In every case previously studied, the effect when $n=1$ is less than four times

FIG. 2.



n = number of equivalents of salt per 100 *grams of anhydrous malic acid.*

that when $n=\frac{1}{4}$, and the corresponding curve is convex upwards. This still holds for magnesium chloride and magnesium nitrate; but for the other salts in table VI, and notably those of zinc and mercury, the reverse is true. A striking illustration is the case of zinc sulphate, where the effect when $n=\frac{1}{4}$ is actually zero, that when $n=1$ being more than a degree. It thus appears that the

first addition of zinc sulphate produces a negative effect, making the rotation more lævo; and that as further quantities are added, the influence attains a negative maximum, passes again through zero, and becomes positive. The case of mercuric nitrate, if comparable, is more remarkable still. The figures (for $n=\frac{1}{4}$, $\Delta=-3\cdot36°$, and for $n=1$, $\Delta=-3\cdot58°$) suggest that the initial large negative influence reaches a maximum between the two concentrations studied, and that further additions of salt would probably influence the rotation in a dextro-sense.

The cause of the greater complexity of the influence of these salts is doubtless connected with their being salts of much weaker bases than those previously studied, the complexity of the influence increasing with the weakness of the base. The incipient formation of feebly dissociated salts or complexes of malic acid appears a probable explanation. Malic acid is noted for its tendency to form with weakly basic metals complexes of a widely different rotation from the acid itself. On the addition to the acid of a salt of a weak base, a limited amount of the feebly dissociated malate or complex would be formed, and equilibrium set up according to the equation:

$$\text{Salt of weak base and strong acid} + \text{malic acid} \rightleftarrows$$
$$\text{Feebly dissociated malate or complex} + \text{strong acid.}$$

Thus, as actually observed, the initial addition of salt would affect the rotation in an anomalous manner, depressing its value if the malate or complex formed were strongly lævorotatory; whilst further additions would affect it more normally. To test this explanation, a rough experiment was performed in the case of the "$n=1$" solution of zinc nitrate and malic acid (table VI), nitric acid being added in successive small equal quantities to the solution, and its effect on the rotation observed. If the above explanation be correct, the first additions of nitric acid should diminish the amount of the feebly dissociated malate or complex, according to the equation, and thus influence the rotation more powerfully in a dextro-direction than subsequent additions, the effect of which would be only the ordinary one of acids on malic acid (see table VIII). That this actually occurred, the following table shows:

TABLE VII.

No. of parts of nitric acid added.	Observed angle of rotation.
0	0·71°
3	0·98
7	1·19
13	1·33
23	1·54

Effect of Acids.

TABLE VIII.

Acid.	n.	d^{20}_{4}.	α^{20}_{D}.	$[\alpha]^{20}_{D}$.	$[\alpha]^{20}_{D}$ for pure acid.	Δ.
HCl	$\frac{1}{4}$	1·0875	−0·105°	−0·25°	−0·97°	0·72°
HCl	0·859	1·105	0·315	0·75	−0·97	1·72
HNO_3	$\frac{1}{4}$	1·089	−0·195	−0·46	−0·96	0·50
HNO_3	1	1·1153	0·255	0·64	−0·96	1·60
H_2SO_4	$\frac{1}{4}$	1·0947	−0·229	−0·54	−1·09	0·55
H_2SO_4	1	1·1385	0·294	0·71	−1·09	1·80
$C_2H_4O_2$	$\frac{1}{4}$	1·0812	−0·432	−1·03	−1·09	0·06
$C_2H_4O_2$	1	1·0855	−0·304	−0·78	−1·09	0·31

Schneider (*Annalen*, 1881, **207**, 278) investigated the effect of sulphuric and acetic acids on a considerably weaker solution of malic acid than that employed in the present research, and found that both changed the rotation in a dextro-sense, the former, however, tenfold more so than the latter. The measurements tabulated above for these acids are in harmony with his result. Acetic acid exerts a regular and positive, but notably small, influence, a fact to which future reference will be made.

Some small part of the influence of the acids must be due to their throwing back the small electrolytic dissociation of the malic acid; but it is as hydrogen salts that they have their chief effect. The latter is, for the mineral acids, regular and somewhat smaller than that of the alkali salts. Hydrochloric acid exerts a less influence than lithium chloride, so that in order of influence K>Na>Li>H, parallel to the order of atomic weights. Nitric acid has less influence than hydrochloric acid, as was to be expected; but sulphuric acid breaks the usual order, $Cl > NO_3 > \frac{1}{2}SO_4$, in that it lies between hydrochloric and nitric acids in its effect. The explanation of this exception is not clear; it may possibly be due to the fact that HSO_4 ions are largely present instead of the SO_4 ions in other sulphate solutions.

Effect of Salts on Solutions of Varying Concentration.

Hitherto the influence of electrolytes has been considered on the specific rotation of 20 per cent. solutions of malic acid only. It was thought of interest to determine how that influence varied, both absolutely and relatively, with respect to different salts when the concentration of the acid was varied. For this purpose the effect of potassium chloride and of sodium chloride was studied on 5 per cent. and 40 per cent., as well as on 20 per cent. solutions of malic acid. In table IX, p = percentage of malic acid solution; n = number of equivalents of salt added per 100 grams of pure malic acid; other symbols have their usual meaning.

TABLE IX.

Salt.	p.	n.	d_4^{20}.	a_D^{20}.	$[a]_D^{20}$.	$[a]_D^{20}$ for pure acid. (a.)	Δ.
KCl	5	$\frac{1}{4}$	1·0235	−0·161°	−1·59°	−2·25°	0·66°
KCl	5	1	1·0405	−0·034	−0·34	−2·25	1·91
KCl	5	4	1·1043	0·335	3·50	−2·25	5·75
NaCl	5	$\frac{1}{4}$	1·023	−0·183	−1·81	−2·25	0·44
(b) KCl	20	$\frac{1}{4}$	1·1013	0·455	1·07	−0·88	1·95
(b) NaCl	20	$\frac{1}{4}$	1·0993	0·30	0·70	−0·97	1·67
KCl	40	$\frac{1}{4}$	1·2132	3·573	3·96	0·535	3·425
NaCl	40	$\frac{1}{4}$	1·2083	3·417	3·74	0·535	3·205

(a) For this column see table I.

(b) These figures are taken from table II.

The relative effect of equivalent quantities of potassium chloride and sodium chloride is seen to be about the same for each strength of acid solution, in each case potassium chloride exercising somewhat more influence than sodium chloride. A similar result may be inferred to hold for the influence of salts generally.

The values of Δ given for the three different concentrations of potassium chloride in the case of 5 per cent. acid solutions show the regularity of the influence exerted, even when (as for $n=4$) the molar concentration of the salt considerably exceeds that of the acid. If these values are considered along with the other results obtained for potassium chloride (tables II and IX) a simple and important relation is seen to obtain between Δ and the potassium chloride concentration of the solutions examined. Let N denote the number of equivalents of potassium chloride per 100 c.c. of solution (p and Δ same as before); then, with the necessary calculations, the following is obtained:

TABLE X.

p.	N.	Δ.
5	0·0128	0·66°
5	0·052	1·91
5	0·221	5·75
20	0·0273	1·04
20	0·055	1·95
20	0·112	3·49
20	0·232	5·57
40	0·121	3·425

It is evident that Δ depends mainly on N, and but little on p; in other words, the influence of the salt on the specific rotation depends mainly on the concentration of the solution with regard to that salt, and not on the concentration of malic acid present. Each malic acid molecule may be regarded as affected independently of other malic acid molecules, but to a degree dependent on the

number of salt molecules or ions within its sphere of influence. What little departure the above table shows from this rule is explicable by the varying malic acid present causing a variation in properties of solvent and salt, for example, by affecting the degree of dissociation. It may be mentioned that Farnsteiner's work on the influence of salts on the rotation of sucrose reveals a quite analogous law (*Ber.*, 1890, **23**, 3750).

Effect of Salts of Weak Acids.

It has been calculated above (p. 2266) that the action of malic acid on salts of strong bases and strong acids is negligible. This would not, however, hold in the case of a salt of a weak acid. It was thought of interest to determine the effect in one or two cases of an acetate, which is the salt of an acid weaker even than malic.

TABLE XI.

Salt.	n.	d^{20}_{4}.	α^{20}_{D}.	$[\alpha]^{20}_{D}$.	$[\alpha]^{20}_{D}$ for pure acid.	Δ.
$KC_2H_3O_2$	$\frac{1}{4}$	1·1000	−0·762°	−1·82°	−0·95°	−0·87°
$KC_2H_3O_2$	1	1·1540	−2·216	−5·74	−0·95	−4·79
$Ba(C_2H_3O_2)_2$......	$\frac{1}{4}$	1·1235	1·26	2·98	−0·97	3·95
$Ba(OH)_2$	0·2435	1·1195	1·069	2·49	−0·97	3·46

For "$n=\frac{1}{4}$" concentration, potassium acetate gave an effect of −0·87°, as against +1·95° for potassium chloride. This negative effect (in contrast with the case of mercuric nitrate) was more than quadrupled on quadrupling the amount of salt added. The contrast between the influence of potassium acetate and that of other potassium salts is explained by the large formation in the former case of hydrogen malate and undissociated acetic acid. The extent and effect of this action may be approximately calculated for the "$n=\frac{1}{4}$" addition of potassium acetate. In the following scheme the symbols mean the same as in the somewhat similar calculation on p. 2266.

$$\begin{array}{ccccc} H\bar{A} & + & KC_2H_3O_2 & \rightleftarrows & K\bar{A} + H{\cdot}C_2H_3O_2 \\ a_1 & & a_2 & & a_3 \qquad a_4 \\ 1-x & & n-x & & x \qquad x \end{array}$$

Let k_1 and k_2 be the respective dissociation constants of malic and acetic acids, and C the concentration of hydrion in solution. The following well-known relations will hold:

$$C \times \{a_1(1-x) + a_3x\} = k_1 \times (1-a_1)(1-x) \quad . \quad . \quad . \qquad \text{(i)}$$

and

$$C \times \{a_2(n-x) + a_4x\} = k_2 \times (1-a_4)x \quad . \quad . \quad . \quad . \qquad \text{(ii)}$$

∴ by division,

$$\frac{a_1(1-x) + a_3x}{a_2(n-x) + a_4x} = \frac{k_1(1-a_1)(1-x)}{k_2(1-a_4)x} \quad . \quad . \quad . \qquad \text{(iii)}$$

Now α_2 may be taken approximately equal to α_3; and α_1, and particularly α_4, are very small. Also, $k_1 = 3{\cdot}95 \times 10^{-4}$, $k_2 = 1{\cdot}8 \times 10^{-5}$. Hence, equation (iii) reduces approximately to:

$$x^2 = \frac{395}{18}\,(1-x)(n-x).$$

Now, as in the former calculation, $n = 0{\cdot}335$.

$\therefore\ x = 0{\cdot}3263$; that is, $\dfrac{0{\cdot}3263}{0{\cdot}335}$ or 97·4 per cent. of the potassium acetate has been acted on and hydrogen malate formed.

An estimate may now be made of the order of the rotation the solution might be expected to show. The rotation should mainly consist of (*a*) the rotation of the potassium hydrogen malate, (*b*) that of the excess of untransformed malic acid, and (*c*) the influence of the potassium hydrogen malate and acetate, similar to that of other salts, on the rotation of the excess of malic acid. For (*a*), interpolation from the data of Schneider (*Annalen*, 1881, **207**, 266), with necessary calculation, gives $-0{\cdot}99°$ as the actual rotation of 200 mm. of a solution of potassium hydrogen malate of the same concentration as has been calculated to be present above. For (*b*), similar interpolation and calculation from the author's data in table I give $-0{\cdot}41°$ as the rotation caused by the residual unchanged malic acid (amounting to 67·4 per cent. of the whole). For (*c*), assuming the influence to be approximately equal to that of an equivalent quantity of potassium chloride, calculation gives 0·55°. Adding these three effects, the observed rotation α of the solution should thus be about $-0{\cdot}99° - 0{\cdot}41° + 0{\cdot}55° = -0{\cdot}85°$. The angle actually observed was $-0{\cdot}76°$. The agreement between the results of calculation and observation is at least sufficiently good to show that the abnormal negative influence of potassium acetate, and even its order of magnitude, might have been anticipated.

Barium salts (table IV) exert so large an influence on the rotation of malic acid that the question suggests itself whether here, at least, the formation of a chemical complex or undissociated salt is accountable. Considering the strongly basic nature of barium, such a thing is a priori improbable; yet the large influence referred to, considered in conjunction with the extraordinarily sharp ascent to a large dextrorotation determined by Schneider for barium malate, even in dilute solution (*loc. cit.*, p. 277), makes it desirable to answer the question with greater certainty. The results for the addition of barium acetate and barium hydroxide, tabulated above, enable this to be done. If a complex or feebly dissociated malate were formed, a much greater effect would be expected in these cases than when the hydrochloric acid is competing for the barium. Tables IV and XI show, however, that, on the contrary, and as in

the case of potassium acetate, the acetate and hydroxide of barium cause considerably less dextrorotation than the chloride.

The table shows that barium hydroxide was added in somewhat smaller proportions than the barium acetate, in fact, so as to produce in solution the amount of barium hydrogen malate which a calculation similar to that made in the case of potassium acetate would show to be formed when the barium acetate was added. As would be expected if the apparent influence of the acetate were due to an almost complete formation of hydrogen malate, the effect of the barium hydroxide was only a little less than that of the barium acetate. The difference of 0·49° is to be explained by (i) the slightly greater amount of barium in the latter case influencing the rotation of the unchanged malic acid by 0·1° to 0·2°; (ii) the one-fourth equivalent of acetic acid present in the latter case exercising (see table VIII) a small effect on the rotation, say, 0·1°; (iii) the more dilute solution in the former case, due to the water of neutralisation; this would rather lower the observed rotation.

Effect of Electrolytes on Malates.

Thomsen (*J. pr. Chem.*, 1887, [ii], **35**, 145) found that excess of alkali had a considerable influence on the rotation of alkali salts of malic and other hydroxy-acids, which he ascribed to the formation of complexes, the excess of alkali combining with the alcoholic hydroxyl. The evidence offered in support does not seem strong, no such complex being prepared, and the main argument apparently being the observed effect on the rotation. It seemed worth investigating whether sodium chloride affected sodium malate similarly to excess of sodium hydroxide. The solutions were prepared of such strength that they may be considered to consist of 20 per cent. malic acid solution, together with the amount of anhydrous sodium hydroxide or chloride required for the equivalent proportions. In the following table, $[\alpha]_D^{20}$ is calculated as the specific rotation of the malic acid present; Δ is the positive increase in $[\alpha]$ due to addition of the extra sodium hydroxide or chloride molecule.

TABLE XII.

Equivalent proportions.	d_4^{20}.	α_D^{20}.	$[\alpha]_D^{20}$.	Δ.
$C_4H_6O_5 + 2NaOH$	1·171	−3·123°	−7·46°	—
$C_4H_6O_5 + 3NaOH$	1·2226	−1·524	−3·67	3·79°
$C_4H_6O_5 + 2NaOH + NaCl$	1·2172	−2·006	−4·97	2·49
*$C_4H_6O_5 + 2NaOH$	1·1716	—	−7·42	—
*$C_4H_6O_5 + 3NaOH$	1·2222	—	−3·71	3·71

* The last two lines are obtained by interpolation and calculation from Thomsen's results; they agree well with the author's data, in the first two lines.

It appears that sodium chloride produces a dextro-effect on the rotation about two-thirds of that produced by sodium hydroxide; thus the influence is at least of the same order; and if, as seems likely, the influence of sodium chloride is not due to a complex, it cannot be said, apart from further evidence, that the influence of sodium hydroxide is so caused. Other substances than sodium hydroxide would presumably similarly influence the rotation of sodium malate. It is interesting to note that, if two molecules of sodium chloride had been first added to the 20 per cent. malic acid instead of two of sodium hydroxide, the third molecule of sodium chloride would, by extrapolation from the results in table II (if such extrapolation can be trusted), have an influence on the rotation of approximately the same magnitude, 2·5°; at any rate, not more.

Discussion of Results and Conclusions.

Inactive electrolytes might influence the rotation of a solution of malic acid in two ways: (i) by affecting the composition or constitution of the active molecules; (ii) by setting in operation solution-forces which would affect the asymmetry of the molecules. Change in composition might come about, in the first place, by the salts forming complexes with the malic acid, an explanation which, with a possible exception in the case of a few of the salts of table VI, may on the following grounds be dismissed as most improbable: (*a*) the regular nature of the salt influence; (*b*) the *a priori* inconceivability of a salt like potassium chloride forming such complexes; and (*c*) the evidence already given against complex formation in the case of barium chloride. Secondly, the malic acid might act on the salts, forming malates and liberating acids; but calculation, confirmed by experiment, has shown that this only occurs to an extent of any importance when the salt of a weak acid, such as acetic, is added; thus, in a solution of malic acid and potassium chloride, the partial formation of potassium hydrogen malate, which is lævorotatory (Schneider, *loc. cit.*, p. 266), could not explain the large dextro-influence observed. Thirdly, change of molecular composition might be due to change of electrolytic or other dissociation in the presence of the salts; but the magnitude of the effects observed is far too great to be explained by change of electrolytic dissociation, whilst it appears highly improbable that polymerisation would be largely influenced by the presence of the salts.

The cause of the salt-influence must, then, be sought elsewhere than in change of composition or constitution of the active substance. An explanation plausible at first sight is that the formation in solution of hydrated molecules by the added salts

would act like concentrating the solution, which is well known to influence the rotation of malic acid in a dextro-sense (Schneider, *loc. cit.*, p. 262). That such an action, if occurring at all, is relatively insignificant, is shown (i) by the fact that the magnitude of the salt-influence is often far too great to be thus explained, barium chloride, for example, producing at the higher concentration an effect several times as great as would be given by total dehydration of the malic acid (assuming Schneider's value of 5·89° for the rotation of the anhydrous acid); (ii) by the fact that, in general, the salts with greatest affinity for water, such as lithium chloride, actually exercise the least influence.

Light would be thrown on the salt-effects could a parallelism be discovered between them and any other physical properties of the solutions. The result of a search made by the author for such a parallelism may be summarised as entirely negative; this applies not only to purely physical properties, such as viscosity and density of the solutions, mass of salt added, etc., but also to the physico-chemical action of salts in precipitating colloids, and their influence on the solubility of non-electrolytes in water (Rothmund, "Löslichkeit und Löslichkeitsbeeinflussung," p. 148). It is specially noteworthy that the internal pressure of aqueous solutions of the various salts (see Tammann, "Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen," p. 87) shows no significant parallelism to the effects of the salts on the rotation of malic acid. This fact bears on Patterson's attempt (Trans., 1901 and following years) to establish a general connexion between the "solvent influence" on rotation and the internal pressure of the solutions.

The above failure to connect the observed effects of electrolytes on the rotation of malic acid with ordinary chemical or physical changes confirms the view that the influence is mainly due to a direct and distinctive power possessed by the inactive molecules in solution to affect the asymmetry of the active ones within their sphere of influence without actual chemical combination. The law deduced on p. 2277 that "the influence of the salt on the specific rotation depends mainly on the concentration of the solution with regard to that salt, and not on the concentration of malic acid," thus receives its explanation. Further, (i) from the additive nature of the effect of strong positive and negative radicles (p. 2272); (ii) from the smallness of the effect of mercuric chloride and acetic acid, the two practically non-ionised substances used; (iii) from the parallelism between unexpectedly low influence and low conductivity in the case of barium nitrate; and (iv) from the consideration that most of the properties of solutions of electrolytes are actually

ionic, it is reasonable to conclude that the large effects tabulated in this paper are chiefly produced by the ions.

The nature of this ionic influence can be little more than surmised. For positive univalent ions the influence is in the order of the electro-affinities in aqueous solution, thus:

$$Cs > Rb > K > Na > Li > H,$$

whilst for negative univalent ions the reverse is the case, thus: $I > Br > Cl > NO_3$. Passing to bivalent ions, this parallelism is broken; $\frac{1}{2}Ba$ and $\frac{1}{2}Ca$ have an influence greatly exceeding that of the more positive Cs; and $\frac{1}{2}SO_4$ less than that of the more negative NO_3. The unexpected place that sulphuric acid was seen to occupy in the order of influence of acids may be due to the univalent HSO_4 ions affecting the rotation much more than SO_4 ions. With the exception, however, of cadmium, which is between zinc and mercury in its electro-affinity, the bivalent metal ions show among themselves a similar parallelism, thus:

$$Ba > Ca\ (> Cd) > Mg > Zn > Hg.$$

This connexion between electro-affinity and ion-influence is striking.

As for the mode of the influence, it appears plausible that it may be connected with the sensitiveness of the alcoholic hydroxyl of malic and other hydroxy-acids, which is liable to be attacked with the formation of complexes showing unusually large rotation. The ions within the sphere of influence of a malic acid molecule may be the centres of forces which, acting on the sensitive hydroxyl group, change the asymmetry or rotatory power of the molecule. If this is the point of influence, malic anions ought to be similarly sensitive to ionic influence—an expectation confirmed by facts (see p. 2281). It is worthy of note that when the hydroxyl group had been attacked and a chemical complex formed, Rosenheim and Itzig (*Ber.*, 1899, **32**, 3432) found that the great sensitiveness of malic acid to changes of concentration disappeared.

If the above view is correct, light is thrown on the general nature of the often otherwise inexplicable influence of solvents on rotation. Without any change of molecular composition or constitution (as usually understood), the interaction of the "residual affinities" of the molecules of solute and solvent may affect the degree of asymmetry of the former, just as malic acid molecules are influenced by neighbouring ions in aqueous solution.

A sidelight of great interest on the above data and discussion has yet to be mentioned. Schneider (*Annalen*, 1881, **207**, 257) measured the specific rotation, $[\alpha]_D^{20}$, in aqueous solutions of various concentration of malic acid, the malates and hydrogen malates of potassium, sodium, lithium and ammonium, and barium malate.

He found the specific rotation of malates to vary with the concentration, even more than that of malic acid. Moreover, the diversity of rotation shown by the various malates (see his diagram, *loc. cit.*, facing p. 368) is not merely due to his plotting specific rotations against percentage compositions of the solution, for when calculations are made from his data, and molecular rotations plotted against molar concentrations, the diversity persists in a no less striking form. This might be expected at higher concentrations of dissolved salt, where the influence of the metallic radicles in the undissociated molecules is naturally felt. The interesting fact is that at lower concentrations the differences in molecular rotation of the various salts persist in such a way that only the barest approximation holds to Oudemans' law, namely, that salts of an active acid and inactive base show the same molecular rotation in very dilute solutions. Schneider's data for barium malate did not allow of extrapolation of any accuracy; the following table shows the values given by him (*loc. cit.*, p. 284), by extrapolation from an empirical formula, for the molecular rotations at infinite dilution of the alkali malates.* The last column shows the corresponding values obtained by the author from graphical extrapolation.

TABLE XIII.

Malate of	$[M]_D^{20}$ at inf. dilution (Schneider).	$[M]_D^{20}$ at inf. dilution (graphically).
KH	−10·65°	−10·4°
NaH	−10·95	−11·0
LiH	−11·87	−12·5
K_2	−15·35	−15·5
Na_2	−17·52	−16·2
Li_2	−18·56	−19·2

The above table shows beyond doubt that, according to Schneider's results, Oudemans' law is only approximately obeyed. In the case of both malates and hydrogen malates, the molecular rotation at infinite dilution of the potassium salt is more dextro- than that of the sodium salt, and the latter than that of the lithium salt, an order of effect remarkably parallel to that given for the salts in table II, namely K>Na>Li. On the view which the author has taken, the explanation is simple. The metallic ions of the dissociated malates retain the power to influence the asymmetry of the malic anion, just as the ions of salts have been seen to affect malic acid molecules and anions (tables II and XII). At infinite dilution this influence persists, for, unlike the case in which the ions of electrolytes influence malic acid molecules by their chance proximity,

* Owing to hydrolysis probably commencing at low concentrations, the figures for the malate of the weak ammonium are not very significant.

the positively charged cations must by electrostatic forces be kept always within the sphere of influence of the negatively charged active anions. Hence if alkali cations influence the rotation of malic or hydromalic anions in the same order (K>Na>Li) as they influence the undissociated molecules, just such deviation from Oudemans' law would be expected as actually observed. It may be added that the rapidly increasing dextrorotation of barium malate is probably due (in part, at least) to the influence on the malic anions of the barions, which have been seen (table IV) to have an extraordinarily great influence on malic acid itself.

If the above view of the invalidity of Oudemans' law in this case is correct, it is evident that colorimetric and other discrepancies cited against the ionic hypothesis may really be an indication of a similar continued mutual influence of the dissociated ions.

The influence of the alkali salts on the rotation of malic acid shows a regularity hitherto unmentioned. In general, the rate of the initial influence of a salt is not sustained, but falls off as its concentration increases. The regularity referred to consists in the fact that the rate of influence of the alkali chlorides, for example, falls off more rapidly the higher the atomic weight of the metal. This is shown in Fig. 2 by the increasing curvature of the curves from lithium chloride to cæsium chloride. No explanation of this behaviour has been found.

In conclusion, it may be said that a systematic confirmation and extension of some of the older work on malic acid and malates seems called for, using purer materials, more accurate instruments, etc. The determination, in very dilute solutions, of the rotation of malates, their electrolytic dissociation, and the effect of various salts on their rotation, would be a valuable contribution to the subject.

Finally, the author is of the belief that electrolytes will exercise a similar influence on tartaric and other hydroxy-acids—a matter perhaps worthy of investigation.

Summary.

(1) Certain other workers (especially Schneider and Woringer) appear to have erred in the determination of the strength of their malic acid solutions, and their data need revision accordingly.

(2) Electrolytes in general exercise a large influence on the rotation of malic acid solutions, turning it in a dextro-direction.

(3) This influence is mainly a specific additive property of the radicles or ions; it is notably great in the case of alkaline earth salts; and it appears to be related with the valency of ions and their order of electro-affinities.

(4) The influence of electrolytes is shown not to be in general due to complex-formation or ionic reaction, or to hydrate-formation by the electrolytes.

(5) The asymmetry of the malic acid molecules is affected by the ions within their sphere of influence, to an extent dependent on the concentration of electrolyte, and not largely on that of malic acid. No connexion has been found with other properties of electrolyte solutions.

(6) Thomsen's supposed complex-formation between sodium malate and excess of alkali appears explicable on the ground of similar ionic influence on the malic anions.

(7) The divergencies of the alkaline malates (according to Schneider's data) from obeying Oudemans' law appear explicable on the ground of the continued influence of the dissociated but necessarily adjacent ion; (the same may hold for other apparent contradictions of the ionic hypothesis).

The author desires to express his indebtedness to Professor F. G. Donnan, whose suggestions and advice were invaluable throughout the course of the work.

THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTROCHEMISTRY,
UNIVERSITY OF LIVERPOOL.

CCLII.—*Organic Derivatives of Antimony. Part II. The Orienting Influence of Antimonic Substituents in the Benzene Nucleus.*

By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT.

PHOSPHORUS, arsenic, and antimony differ markedly from nitrogen, the initial member of this periodic family of elements, in regard to the degree of hydration exhibited by their oxy-acids, and this difference persists in the organic derivatives of these acids. Nitric acid, which yields metallic salts derived from the meta-hydrate, $HO{\cdot}NO_2$, gives rise to organic nitro-compounds corresponding exclusively with its least hydrated form. On the contrary, the organic derivatives of phosphorus, arsenic, and antimony, like the metallic salts of the oxy-acids of these elements, exhibit types corresponding with the more hydrated pyro- and ortho-acids, as well as compounds derived from the meta-acids.

Accordingly these three elements can each furnish three series

of compounds derived from their ortho-oxy-acids, as illustrated in the following scheme, where X is phosphorus, arsenic, or antimony, and R a univalent alkyl or aryl group:

$$\begin{array}{ccc} HO{\cdot}XO(OH)_2 & (HO)_2XO{\cdot}OH & (HO)_3X{:}O \\ \downarrow & \downarrow & \downarrow \\ R{\cdot}XO(OH)_2 & R_2XO{\cdot}OH & R_3X{:}O \end{array}$$

Some of the compounds of the third series are found to exist in the hydrated form, $R_3X(OH)_2$, which corresponds with the true ortho-hydrate, $X(OH)_5$.

When substitution occurs in nitrobenzene the introduction of the entrant substituent follows the meta-law of substitution. Nitration and sulphonation, for example, lead mainly to the production of *m*-dinitrobenzene and nitrobenzene-*m*-sulphonic acid. In this respect the nitro-group is analogous to the carboxyl and sulphonic groups, which are similarly derived from meta-acids:

meta-Acids.	Phenyl compound.	1 : 3-Di-derivative.
$HO{\cdot}NO_2$	$C_6H_5{\cdot}NO_2$	$C_6H_4(NO_2)_2$
$HO{\cdot}CO_2H$	$C_6H_5{\cdot}CO_2H$	$C_6H_4(NO_2){\cdot}CO_2H$
$HO{\cdot}SO_3H$	$C_6H_5{\cdot}SO_3H$	$C_6H_4(NO_2){\cdot}SO_3H$

This being the behaviour of meta-acidic groups in reactions involving substitution, it becomes of interest to ascertain what law of substitution is followed in the presence of such acid groups as $\cdot XO(OH)_2$, $:XO{\cdot}OH$, and $\vdots X{:}O$ or $\vdots X(OH)_2$.

Although a very large amount of work has been carried out, chiefly by Michaelis and his pupils, on aromatic compounds containing phosphoric, arsenic, and antimonic substituents, yet the influence of these groups on the orientation of entrant radicles has not been studied systematically; for example, in the phosphorus series it is surmised that, in nitrophenylphosphinic acid, the nitro-group enters a meta-position with respect to the phosphoric radicle (Michaelis and Benzinger, *Annalen*, 1877, **188**, 273), but in the case of trinitrotriphenylphosphine oxide the nitro-groups are assumed to take up para-positions (Michaelis and Soden, *Annalen*, 1885, **229**, 326). Some uncertainty still exists in regard to the arsenic series, although recent researches on atoxyl and allied compounds have shown that the nitration product of phenylarsinic acid is the meta-compound (Michaelis and Lösner, *Ber.*, 1894, **27**, 263; Bertheim, *ibid.*, 1908, **41**, 1655; 1911, **44**, 3297).

The organic antimony derivatives have recently acquired importance owing to the belief that some of these substances might prove to be of therapeutic interest. The present communication deals mainly with the nitration of the three series of antimony compounds and with the orientation of the products.

(1) *Monophenyl Series.*—An interesting point has arisen in connexion with the preparation of phenylstibine dichloride, the starting point in this series. The dichloride was first prepared by Hasenbäumer (*Ber.*, 1898, **31**, 2910) by heating triphenylstibine and antimony trichloride in xylene at 240°. In a recent communication Michaelis and Günther (*Ber.*, 1911, **44**, 2316) state that this reaction leads to the formation of diphenylstibine chloride, which they isolated in comparatively poor yield. We find that both these observations are correct, our experiments showing that the condensation is a balanced reaction in the sense indicated by the following equations:

$$2(C_6H_5)_3Sb + SbCl_3 = 3(C_6H_5)_2SbCl,$$
$$(C_6H_5)_2SbCl + SbCl_3 \rightleftharpoons 2C_6H_5\cdot SbCl_2.$$

Phenylstibine dichloride, which according to our experience is the main product of the foregoing change, yields phenylstibinic acid on successive chlorination and hydrolysis. The nitration product of this acid consists chiefly of m-*nitrophenylstibinic acid*, for on heating at 110—120° with phosphorus pentabromide (3 mols.) the antimonic group is eliminated, and 1-bromo-3-nitrobenzene is produced:

$$NO_2\cdot C_6H_4\cdot SbO(OH)_2 + 3PBr_5 = NO_2\cdot C_6H_4\cdot SbBr_4 + 3POBr_3 + 2HBr.$$
$$NO_2\cdot C_6H_4\cdot SbBr_4 = NO_2\cdot C_6H_4Br + SbBr_3.$$

This result might have been predicted by applying the Crum Brown and Gibson rule. The hydrogen derivative of the antimonic substituent is $H\cdot SbO(OH)_2$, assuming this to be a possible form of antimonious acid. Now since this acid is directly oxidisable to antimonic acid, the corresponding radicle, $\cdot SbO(OH)_2$, like the NO_2 and CO_2H groups, should induce substitution in the meta-position. The groups $\colon SbO\cdot OH$ and $\vdots SbO$ or $\vdots Sb(OH)_2$ are present in the diphenyl and triphenyl series, and since the corresponding hydrogen compounds are unknown, it is impossible to predict what would be their behaviour towards oxidising agents. Accordingly the rule cannot be applied to these cases.

(2) *Diphenyl Series.*—The nitration product of diphenylstibinic acid is rather more stable than *m*-nitrophenylstibinic acid and the trinitro-derivative of triphenylstibinic acid, but on heating at 150—160° with phosphorus pentabromide (2 mols.) and bromine (1 mol.) it undergoes fission into antimony bromide and 1-bromo-3-nitrobenzene:—

$$(NO_2\cdot C_6H_4)_2SbO\cdot OH + 2PBr_5 = (NO_2\cdot C_6H_4)_2SbBr_3 + 2POBr_3 + HBr.$$
$$(NO_2\cdot C_6H_4)_2SbBr_3 + Br_2 = 2NO_2\cdot C_6H_4Br + SbBr_3.$$

The group $:SbO \cdot OH$ accordingly induces substitution of a NO_2 radicle in the meta-position.

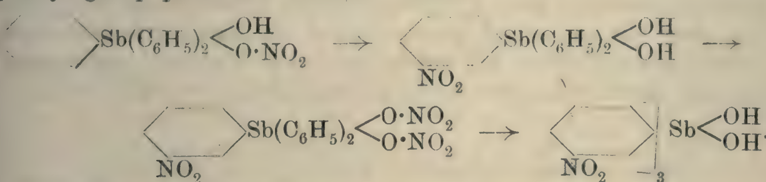
(3) *Triphenyl Series.*—Triphenylstibinic acid (triphenylstibine dihydroxide) furnishes a trinitro-derivative, which is proved to be chiefly the meta-compound by fission at 110° with phosphorus pentabromide (2 mols.) and bromine (2 mols.):

$$(NO_2 \cdot C_6H_4)_3Sb(OH)_2 + 2PBr_5 = (NO_2 \cdot C_6H_4)_3SbBr_2 + 2POBr_3 + 2HBr.$$

$$(NO_2 \cdot C_6H_4)_3SbBr_2 + 2Br_2 = 3NO_2 \cdot C_6H_4Br + SbBr_3.$$

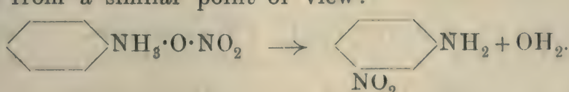
The 1-bromo-3-nitrobenzene collected was about 70—80 per cent. of the calculated quantity.

In the triphenyl series it is of interest to note that intermediate nitration products can be isolated when less concentrated nitric acid is employed. Triphenylstibine nitrate and hydroxynitrate have both been described, and it is therefore probable that the first stage of nitration in these three series of stibinic acids is the formation of nitrates, the nitro-group becoming first attached to an oxygen of the antimonic substituent, and subsequently migrating into the ring in the meta-position, this process being repeated until each phenyl group present is nitrated:



Cases in which the migrating group passes from the side-chain to a meta-position in the ring are very uncommon, but an interesting comparison may be drawn between the foregoing nitrations and the transformation of benzoyl nitrate into *m*-nitrobenzoic acid:

(Francis, *Ber.*, 1906, **39**, 3798). The production of *m*-nitroaniline from aniline nitrate and concentrated sulphuric acid may be regarded from a similar point of view:



Experimental.

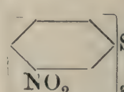
Triphenylstibine, the starting point of this investigation, was first prepared by Michaelis and Reese in the interaction of antimony

trichloride, chlorobenzene, and sodium in dry benzene (*Annalen*, 1886, **233**, 39), and since produced by Pfeiffer through the Grignard reaction (*Ber.*, 1904, **36**, 4620), the yield being about 60 per cent of the weight of trichloride employed.

The following modified process gave an almost quantitative yield of this substance. A 10 per cent. benzene solution containing 18 grams of antimony trichloride was slowly added to the Grignard reagent prepared from 50 grams of bromobenzene and 7·2 grams of powdered magnesium suspended in dry ether, and the mixture boiled for six hours and then distilled in steam. The fusible organic residue was freed from diphenyl by extraction with small quantities of cold alcohol, and the undissolved triphenylstibine (m. p. 48°) was further purified by crystallisation from hot alcohol, although this treatment was not generally necessary.

A similar result was obtained by using antimony tribromide, but the sparing solubility of this halide in benzene necessitated the employment of more dilute solutions.

If in these condensations with antimony trichloride or tribromide the benzene solution is filtered from the precipitate of magnesium compounds and worked up without distillation in steam, the product consists in part of triphenylstibine dichloride or dibromide, but these compounds of quinquevalent antimony are convertible into triphenylstibine by reduction with alcoholic ammonium sulphide as recommended by Kaufmann (*Ber.*, 1908, **41**, 2762).

Tri-m-*nitrotriphenylstibinic Acid*,  Sb(OH)$_2$.

The nitration experiments were carried out on triphenylstibine hydroxynitrate, a compound already described as resulting from the interaction of triphenylstibine dichloride and silver nitrate (Trans., 1910, **97**, 35). This crystalline hydroxynitrate can also be prepared by adding triphenylstibine to a 30 per cent. solution of fuming nitric acid in glacial acetic acid. Nitrous fumes are evolved, and after the violent reaction has subsided, the liquid is gently warmed and poured into water. The recrystallised hydroxynitrate melts at 220°.

Twenty-five c.c. of nitric acid (D 1·5) decolorised with carbamide were mixed with 6 c.c. of concentrated sulphuric acid and maintained at 40° while 3 grams of the hydroxynitrate were slowly added, the temperature being afterwards raised to 55°. After two hours the cooled solution was poured on ice, the precipitated nitro-compound dissolved in warm *N*-sodium hydroxide, and reprecipitated by hydrochloric acid.

Tri-m-*nitrotriphenylstibinic acid* is a pale orange-yellow powder, crystallisable from glacial acetic acid in light yellow leaflets. Its decomposition point is somewhat indefinite, ranging in different preparations from 170° to 191°. This variation is possibly due to the presence of varying amounts of para- and ortho-isomerides. The compound is, however, identical with the substance obtained by May on nitrating triphenylstibine (Trans., 1910, **97**, 1958), this being demonstrated by comparative experiments on the two methods of preparation.

The alkali salts of tri-*m*-nitrotriphenylstibinic acid are soluble in water to a brownish-orange solution, which on boiling acquires an odour of nitrobenzene. The barium, strontium, calcium, magnesium, copper, silver, cobalt, and lead salts obtained by double decomposition from the soluble alkali and ammonium salts are all sparingly soluble.

Orientation Experiments with Tri-m-*nitrotriphenylstibinic Acid.*—Preliminary trials with aqueous potassium hypobromite showed that the acid is oxidised destructively by this reagent. Heating with iodine chloride in glacial acetic acid solution effected the elimination of antimony, but the mixed iodo- and chloro-derivatives of nitrobenzene which were simultaneously produced could not be separated and identified.

(1) One gram of tri-*m*-nitrotriphenylstibinic acid was heated for twelve hours at 115—130° with 15 c.c. of chloroform saturated with hydrogen bromide. The contents of the tube were distilled in steam, but no nitrobenzene could be detected. This experiment, which was duplicated, showed that hydrogen bromide alone did not decompose the nitro-compound into antimony tribromide and nitrobenzene.

(2) A sealed tube containing 1 gram of nitro-acid, 2 grams of phosphorus pentabromide, and 1 gram of bromine in 15 c.c. of chloroform was heated at 130—160°, and although some charring occurred, the yield of 1-bromo-3-nitrobenzene was 70 per cent. of the calculated quantity.

(3) One gram of nitro-acid and 3 grams of bromine heated in chloroform at 115—130° gave on distilling in steam 0·7 gram of 1-bromo-3-nitrobenzene, and 0·25 gram of the unchanged nitro-compound was recovered; the eliminated antimony was precipitated and weighed as sulphide, the calculated amount being obtained.

(4) Experiment 2 was repeated, using dry sodium tri-*m*-nitrotriphenylstibinate instead of the free acid, and adding triethylamine to fix the hydrogen bromide produced during the decomposition. The contents of the tube were distilled in steam, when the only volatile product obtained was 1-bromo-3-nitrobenzene.

(5) Two grams of tri-*m*-nitrotriphenylstibinic acid, 5 grams of bromine, and 15 c.c. of water were heated for several days at 100°, and then for twenty-seven hours at temperatures ranging from 150° to 270°. The product when freed from excess of bromine and distilled in steam yielded 1·2 grams of 1-bromo-3-nitrobenzene, and the residue gave 0·3 gram of brominated product, probably 1:3:4-tribromo-5-nitrobenzene (m. p. 119°).

(6) The crude tri-*m*-nitrotriphenylstibinic acid when boiled with excess of *N*-sodium hydroxide furnished a small amount of nitrobenzene arising probably from the hydrolysis of the para- and ortho-isomerides of this acid, which are not present to the extent of more than 10 per cent.

Tri-m-*aminotriphenylstibine*, $Sb(C_6H_4 \cdot NH_2)_3$.

Two grams of tri-*m*-nitrotriphenylstibinic acid were slowly introduced into 100 c.c. of boiling alcohol containing 5 grams of zinc dust and 0·8 gram of ammonium chloride. The mixture was heated and shaken for half an hour, and then filtered into 100 c.c. of ice-cold water. The precipitated base was dissolved in dilute hydrochloric acid, and the *tri*-m-*aminotriphenylstibine* set free by ammonia:

0·1858 gave 0·3727 CO_2 and 0·0811 H_2O. C=54·69; H=4·85.
0·1030 „ 0·2039 CO_2 „ 0·0455 H_2O. C=54·00; H=4·91.
0·2542 „ 22·8 c.c. N_2 at 24·5° and 760 mm. N=10·03.
0·2654 „ 0·1006 Sb_2O_4. Sb=29·93.

$C_{18}H_{18}N_3Sb$ requires C=54·54; H=4·54; N=10·6; Sb=30·30 per cent.

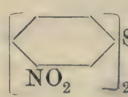
Tri-*m*-aminotriphenylstibine is obtained in colourless crystals from glacial acetic acid only with considerable difficulty; it decomposes indefinitely at about 80°. The base dissolves sparingly in alcohol or water, and is but slightly soluble in acetone, benzene, and other volatile organic media.

The crystalline *hydrochloride*, $Sb(C_6H_4 \cdot NH_2,HCl)_3$, is readily soluble in alcohol or water, but is precipitated from the latter by concentrated hydrochloric acid. Aqueous solutions of the salt are acid to litmus. The base and its salts, either in the solid state or in hot solutions, have a curious pungent odour, and cause violent fits of sneezing.

The hydrochloride was examined physiologically by Dr. Plimmer and by Mr. Hindle; it has a certain trypanocidal power, but nothing like so strong as lithium antimonyl tartrate, and its irritant effects are very acute, causing ulceration at the point of injection.

The base forms the following sparingly soluble salts: picrate, platinichloride, and diazonium chloride; the last of these condenses with alkaline β-naphthol to form an insoluble, red azo-compound. The base itself in neutral or acetic acid solution couples with diazobenzenesulphonic acid to produce a soluble azo-colouring matter.

Under the most favourable conditions the reduction of tri-*m*-nitrotriphenylstibinic acid does not proceed quite smoothly, being accompanied by elimination of antimony from combination with the organic groups. This destructive reduction becomes more pronounced when tin and hydrochloric acid are employed, and a considerable amount of aniline is produced. Tri-*m*-aminotriphenylstibine is not the sole product, as both reducing agents give rise to another basic substance which is soluble in alkali hydroxides as well as in acids; this product, which was not obtained crystalline and has no melting point below 230°, may possibly be tri-*m*-aminotriphenylstibine hydroxide.

*Di-*m*-nitrodiphenylstibinic Acid,*  SbO·OH.

The process employed by Michaelis and Reese (*loc. cit.*) for the preparation of diphenylstibine trichloride was adopted with slight modifications. Antimony trichloride (48 grams) and chlorobenzene (48 grams) dissolved in 150—200 c.c. of dry benzene were added in the cold to 20 grams of sodium which had been previously granulated by melting and shaking under boiling toluene. When a vigorous reaction did not take place spontaneously, it was started by cautiously warming the mixture. After twenty-four hours the solution was filtered from precipitated antimony and unaltered sodium; the benzene and toluene were evaporated away, the oily residue triturated with alcoholic hydrochloric acid till it solidified, and then dissolved in the minimum amount of boiling alcohol. The major portion of the triphenylstibine dichloride (m. p. 141°) crystallised out on cooling, and the mother liquor was concentrated until a second crop of crystals separated. This fraction, which consisted of impure diphenylstibine trichloride, was purified by extraction with hot dilute hydrochloric acid. The acid solution filtered from undissolved triphenylstibine dichloride deposited on cooling lustrous, colourless, lath-like crystals of diphenylstibine trichloride (m. p. 176°). This preparation was repeated several times, and the yields of diphenylstibine trichloride varied from 11 to 16 per cent. of the weight of antimony trichloride employed.

For purposes of nitration the trichloride was dissolved in alcohol, and converted, by means of silver nitrate, into a basic nitrate,

crystallising in clusters of lustrous, colourless needles, and decomposing at 206° with evolution of nitrous fumes.

Four grams of this basic nitrate were added to 56 c.c. of nitric acid (D 1·5) mixed with 20 c.c. of concentrated sulphuric acid; the temperature was maintained at 40°, and afterwards raised to 55°. The clear, yellow solution was then cooled, and poured on to ice; the pale yellow product was dissolved in *N*-sodium hydroxide, and reprecipitated by acetic or hydrochloric acid:

0·2925 gave 18·0 c.c. N_2 at 29° and 768 mm. N = 6·78.
0·3248 „ 0·1254 Sb_2O_4. Sb = 30·48.

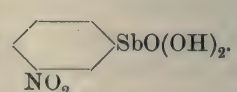
$C_{12}H_9O_6N_2Sb$ requires N = 7·05; Sb = 30·22 per cent.

When crystallised from glacial acetic acid, *di*-m-*nitrodiphenylstibinic acid* separated in radiating clusters of flattened needles, which decomposed somewhat indefinitely at 212°. The nitration product before dissolving in aqueous alkali decomposes at 220—235°, evolving nitrous fumes; it probably consists, at least in part, of a nitrate or basic nitrate.

Di-m-*nitrodiphenylstibinic acid* is insoluble in water, alcohol, or benzene; its alkali salts are soluble in water to an orange-yellow solution; the other metallic salts obtained by double decomposition are very sparingly soluble.

Orientation Experiments.—Preliminary trials showed that di-*m*-nitrodiphenylstibinic acid was more stable than tri-*m*-nitrotriphenylstibinic acid. Sealed tubes containing the dinitro-acid, phosphorus pentabromide (2 mols.), and bromine (1 mol.) were heated at 100°, 125°, and 130—160°. At the two lower temperatures no change occurred, but after heating for eight to nine hours at the highest temperature the organic antimony compound was decomposed, and on distilling in steam the product yielded 1-bromo-3-nitrobenzene (m. p. 56°). The residue consisted of antimony oxybromide and a small amount of viscid decomposition product.

The experiment at 130—160° was repeated with phosphorus pentabromide alone with a similar result; the volatile product was 1-bromo-3-nitrobenzene, and rather more tar was left in the residue.

m-*Nitrophenylstibinic Acid*, 

Phenylstibine dichloride, the starting point in the preparation of monophenylated antimony compounds, was first prepared by Hasenbäumer (*loc. cit.*), and considerable quantities of this material were obtained by his process, which, however, was found to give diphenylstibine chloride as a by-product (Michaelis and Günther, *loc. cit.*).

A series of sealed tubes each containing 5 grams of triphenylstibine, 6·5 grams of dry antimony trichloride, and 12 c.c. of xylene dried over sodium was heated for forty-eight hours at 240°; the liquid contents of the tubes were filtered from a black, insoluble impurity, shaken three times with dilute hydrochloric acid, dried over calcium chloride, and distilled up to 200° under the ordinary pressure. The oily residue was then fractionated under considerably diminished pressure (about 5—7 mm.), when about three-fourths of the material distilled between 160° and 200°, and the remainder was collected between 200° and 240°. Twenty-four grams of triphenylstibine yielded an equal weight of the lower, and about 6—7 grams of the higher, fraction; the latter, which consisted mainly of diphenylstibine chloride, soon solidified, and the crystals then melted at 60°, the melting point being raised to 68° after draining. The more volatile fraction, which consisted mainly of phenylstibine dichloride mixed with a smaller proportion of diphenylstibine chloride, either remained viscid or deposited crystals of the main constituent, which after draining melted at 55—58°.

Each of the foregoing fractions was suspended in dry cooled ether and treated with chlorine. In both cases the solution deposited colourless crystals, but whereas the crystals from the lower fraction melted at the ordinary temperature to a viscid oil, those from the higher fraction remained solid, and after crystallisation from dilute hydrochloric acid melted at 176°, and were thus identified as diphenylstibine trichloride.

The oily chlorine additive compound, consisting of impure phenylstibine tetrachloride, was hydrolysed with aqueous ammonia, when a solid residue was produced and identified as diphenylstibinic acid by conversion into diphenylstibine trichloride (m. p. 176°) by dissolving in hot alcoholic hydrochloric acid. The ammoniacal solution, which contained the greater part of the product of hydrolysis, was acidified with hydrochloric acid, when phenylstibinic acid was precipitated.

The solid chlorine additive compound was also hydrolysed by prolonged digestion with aqueous ammonia, when the greater part of the material remained undissolved, and was identified as diphenylstibinic acid. The ammoniacal filtrate when neutralised yielded a small quantity of phenylstibinic acid.

The Behaviour of Diphenylstibinic Acid towards Aqueous Alkalis.—Inasmuch as phenylstibinic acid is soluble in ammonia or aqueous sodium carbonate as well as in sodium hydroxide solution, and diphenylstibinic acid is described as being soluble in aqueous sodium hydroxide, but not in ammonia or sodium carbonate

solutions, these differences might serve to effect the separation of the two acids in the mixtures obtained in the foregoing experiments. However, the behaviour of diphenylstibinic acid is not invariable in this respect, and its solubility in alkalis depends on the mode of formation.

Diphenylstibine trichloride was dissolved in alcohol and treated with dilute ammonia, when a granular precipitate was obtained insoluble in aqueous ammonia or sodium carbonate. Another portion of this trichloride was dissolved in aqueous sodium hydroxide, and the solution acidified with acetic acid; the diphenylstibinic acid thus precipitated is readily soluble in aqueous ammonia or sodium carbonate.

These two preparations are in all probability differently hydrated modifications of diphenylstibinic acid, the less soluble form being possibly the meta-compound, $Ph_2SbO{\cdot}OH$, whilst the more soluble product may be either the ortho- or pyro-compound.

Nitration of Phenylstibinic Acid.—Three grams of this acid were nitrated in 27 c.c. of pure nitric acid (D 1·5) and 9 c.c. of concentrated sulphuric acid, the temperature ranging from 40° to 55°. The cooled solution when poured on to ice gave a yellow precipitate, which probably consists in part of a nitrate or basic nitrate, since on heating it decomposes with the evolution of nitrous fumes. This product was dissolved in dilute aqueous sodium hydroxide, and m-*nitrophenylstibinic acid* precipitated as a pale yellow compound on acidifying with acetic or hydrochloric acid. The acid dissolves in glacial acetic acid, but does not crystallise at all readily; it has no melting point below 290°:

0·3232 gave 13·7 c.c. N_2 at 27° and 760 mm. N = 4·68.

0·3814 „ 0·1976 Sb_2O_4. Sb = 40·91.

$C_6H_6O_5NSb$ requires N = 4·79; Sb = 41·10 per cent.

Orientation Experiments.—One gram of *m*-nitrophenylstibinic acid, suspended in 15 c.c. of chloroform with 6 grams of phosphorus pentabromide, was heated at 100—110° for four hours, and the product then distilled in steam; 1-bromo-3-nitrobenzene was obtained, the yield being about 70 per cent. of the calculated amount. The residue contained a small quantity of tar.

Triphenylstibinedihydroxidetrisulphonic Acid.

The sulphonation of triphenylstibine dihydroxide proceeds less smoothly than that of the previously described triphenylstibine hydroxysulphate (Trans., 1910, **97**, 37), and accordingly the latter compound was generally employed for this purpose. Triphenylstibine dichloride sulphonates, evolving hydrogen chloride, but the

use of this dichloride offers no advantages. May's experiments (Trans., 1910, **97**, 1958) show that the sulphonation of triphenylstibine itself is not a practicable operation, since the base acts as a reducing agent towards concentrated sulphuric acid, and becomes converted into triphenylstibineoxide sulphate.

Eight grams of the hydroxysulphate mixed with 20 c.c. of concentrated sulphuric acid were treated with 20 c.c. of fuming sulphuric acid (25 per cent. SO_3), the mixture heated at 100° for two to three hours, after which another 20 c.c. of fuming acid were added. The solution was left for twelve hours, poured on to ice, and the liquid neutralised with barium carbonate. The filtrate, freed from barium by the cautious addition of dilute sulphuric acid, was concentrated until of oily consistence, when alcohol produced a white precipitate. The filtrate was further concentrated, and treated repeatedly with alcohol and ether until a white deposit was no longer obtained. The final filtrate on evaporation left a clear, yellow oil, which was washed repeatedly with ether and dried over phosphoric oxide in a vacuum desiccator. Finally, a brittle, yellow mass was obtained resembling amber, the yield being about 40 per cent. of the weight of hydroxysulphate:

0·1806 gave 0·2068 CO_2 and 0·0600 H_2O. C=31·23; H=3·69.
0·4392 „ 0·5128 CO_2 „ 0·1112 H_2O. C=31·84; H=2·81.
0·1864 „ 0·0478 Sb_2S_3. Sb=18·32.
$C_{18}H_{23}O_{14}S_3Sb$ requires C=31·80; H=3·3; Sb=17·67 per cent.

These numbers agree with the formula:

$$(HO)_2Sb(C_6H_4{\cdot}SO_3H)_3,3H_2O;$$

the values for sulphur (16·0) were less concordant (theory=14·14 per cent.), showing that the compound still contains a small amount of more highly sulphonated organic compounds, but owing to the very soluble hygroscopic nature of the acid further purification could not be effected.

When titrated with standard sodium hydroxide and phenolphthalein, the compound was found to have a molecular weight of 687, on the assumption that it is a tribasic acid, the molecular weight calculated from the above formula being 679.

The metallic salts of triphenylstibinedihydroxidetrisulphonic acid are soluble in water; the sodium salt when triturated successively with phosphorus pentachloride and water yields a hydroxy-chloride, $(C_6H_4{\cdot}SO_2Cl)_3SbCl{\cdot}OH$, which dissolves in benzene, and is precipitated therefrom by light petroleum as a granular powder, decomposing indefinitely at 110°:

0·1280 gave 0·1072 AgCl. Cl=20·72.
$C_{18}H_{13}O_7Cl_4Sb$ requires Cl=20·32 per cent.

The white substances precipitated by alcohol or by a mixture of this solvent and ether during the evaporation of solutions of the foregoing trisulphonic acid were found to be mixtures produced by the condensation of antimonic acid and benzenemono- and di-sulphonic acids, their formation being the sequel to the destructive action of concentrated sulphuric acid on the organic antimony compound.

One of these products was prepared synthetically by heating together an aqueous suspension of antimonic acid and benzenesulphonyl chloride. The latter compound underwent hydrolysis; the antimonic and benzenesulphonic acids condensed to yield a soluble compound, which was deposited as a white, microcrystalline precipitate on adding alcohol to the concentrated aqueous solution. This compound, which may be regarded as a complex anhydride of the two acids, is readily soluble in water to a faintly acid solution, and contains about 29 per cent. of antimony and 18 per cent. of sulphur.

Physiological experiments by Dr. Plimmer showed that even in fatal doses triphenylstibinedihydroxidetrisulphonic acid and the above-mentioned benzenesulphonylantimonic acid derivatives did not act as effective trypanocides.

We desire to express our thanks to Mr. G. S. Whitby, B.Sc., A.R.C.S., who collaborated in the earlier experiments, and to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

Royal College of Science, London,
South Kensington, S.W.

CCLIII.—*The Preparation of the Ketones of the Higher Fatty Acids.*

By Thomas Hill Easterfield and Clara Millicent Taylor (New Zealand Government Research Scholar).

The distillation of barium and calcium salts, although of general application as a method for obtaining ketones, suffers from the drawbacks that large quantities of salt cannot be conveniently treated in one operation, and that the yield of ketone is often unsatisfactory. Krafft (*Ber.*, 1882, **15**, 1712) has shown that with fatty acids of high molecular weight the yield is improved by

heating the salts under diminished pressure, and Young (Trans., 1891, **59**, 621) obtained no less than 80 per cent. of the theoretical yield of the ketone of phenylacetic acid by controlling the temperature at which the calcium salt was decomposed, and ensuring the rapid removal of the volatile products of the reaction. Kipping (Trans., 1890, **57**, 532) obtained a 40 per cent. yield of stearone by heating stearic acid with phosphoric oxide. This very convenient method is, however, inapplicable to the higher unsaturated fatty acids. The observation (Easterfield and Bagley, Trans., 1904, **85**, 1244) that in the presence of iron filings abietic acid is readily deprived of its carboxyl group with formation of a hydrocarbon suggested that iron filings might determine the formation of ketones from fatty acids at comparatively low temperatures. This is actually the case with the acids from lauric to melissic acid; thus stearic acid gave an 80 per cent. yield of stearone when heated with powdered cast-iron turnings to 360—370° for a period of three hours.

The hitherto undescribed ketones of the higher fatty acids can be prepared by the same process, but owing to decomposition the yield is not so good.

There can be little doubt that a ferrous salt is first formed, and that this then undergoes decomposition. Ferrous stearate heated to 360° slowly decomposes, and yields about 60 per cent. of stearone.

No satisfactory yield of ketone was obtained by the interaction of iron turnings and acetic, butyric, phenylacetic, benzoic, suberic, and sebacic acids, or with the acid ester of sebacic acid.

The observation that ketones may result by the interaction of acids and metals was first made by Liebig and Pelouze, who obtained acetone by passing the vapour of acetic acid through a heated iron tube, but obtained negative results when a porcelain tube was employed. Jahn (*Ber.*, 1880, **13**, 2107) obtained acetone and impure butyrone respectively by passing the vapours of the corresponding acids over heated zinc dust. Hébert (*Compt. rend.*, 1903, **136**, 682) obtained a mixture of stearone with solid and liquid hydrocarbons by distilling stearic acid with magnesium powder at as low a temperature as possible. Finally, Mailhe (*Bull. Soc. chim.*, 1909, [iv], **5**, 616) found that ketones are the chief products of the interaction of the vapours of the lower fatty acids, from acetic to nonoic acid, with many reduced metals, including such feebly electropositive metals as lead and copper, which in the form of ordinary filings are almost without action on the fatty acids.

The formation of stearone by the action of iron on stearic acid probably accounts for the fact recorded by P. W. Robertson (*Trans. N. Z. Inst.*, 1904, 576) that the last runnings in the commercial

distillation of stearin are so rich in stearone that the melting points of successive portions of the distillate fall rapidly to a eutectic and then rise with even greater rapidity. Examination of the higher distillates obtained in the refining of "distillation" olein shows that they similarly contain oleone.

Experimental.

Preparation of Stearone.—Pure stearic acid was heated with one-tenth of its weight of sifted, clean cast-iron turnings to 280°, at which temperature the evolution of carbon dioxide became perceptible. The temperature was then raised slowly to 360°, and maintained between 360° and 370° for two hours. After removal of the iron and free acid, the ketone was twice crystallised from light petroleum (b. p. 100—120°), with the addition of animal charcoal, and it then melted at 88°. (Found, C = 82·71; H = 14·01. Calc., C = 83·00; H = 13·83 per cent.) The yield of crude stearone melting at 85° was 80 per cent. of that demanded by theory.

In dealing with large quantities of stearic acid it is advisable to raise the temperature rapidly to about 300°, and then to be very cautious about the further rise of temperature, as a sudden frothing sometimes commences at 320—330°.

The following table shows the comparative yields of stearone in a series of experiments made with the object of ascertaining the most suitable conditions of reaction. Column 1 gives the quantity of iron employed, expressed in terms of that theoretically required for the conversion of the whole of the acid into ferrous stearate. Columns 2, 3, and 4 give the percentage of the theoretical yield of ketone formed at the temperature indicated.

Percentage of iron.	Yield at 330°.	Yield at 360°.	Yield at 365°.
100	53	62	80
66	35	53	74
33	3	34	—
20	—	28	—

Unaltered iron remained in the experiments in column 4, and increase in the relative quantity of iron beyond the theoretical quantity did not improve the yield of ketone.

The experiments were carried out as follows: Test-tubes containing 1 gram of stearic acid and the requisite quantity of powdered cast-iron turnings were heated in a Lothar Meyer air-bath for three hours, the last 50° rise of temperature being allowed to occupy one hour, at the end of which time the evolution of carbon dioxide had practically ceased. The product was treated with acid and alkali, and then once crystallised from alcohol, weighed, and the

melting point taken. In no case did the melting point differ by more than 4° from that required for the pure ketone. Very little ketone is formed if stearic acid or calcium stearate is heated to 360° or if stearic acid is heated with metallic iron at temperatures below 300°.

A sample of ferrous stearate prepared by adding ferrous acetate solution to an alcoholic solution of sodium acetate gave on analysis: Fe = 8·9. Calc., Fe = 9·0 per cent. This was heated to 360° for three hours, and the mass extracted with boiling alcohol; a 60 per cent. yield of stearone was obtained. Manganese stearate under similar conditions yielded 42 per cent. of ketone.

Good yields, up to 65 per cent., have been obtained by substituting aluminium and manganese for iron in the above operation.

Diheptadecylcarbinol, $(C_{17}H_{35})_2CH{\cdot}OH$.

The attempt to reduce stearone by means of ethyl alcohol and a very large excess of metallic sodium was unsuccessful, practically the whole of the ketone being recovered unchanged. Even with sodium and boiling amyl alcohol the reduction takes place but slowly.

One gram of stearone was dissolved in 200 c.c. of boiling amyl alcohol, and 8 grams of sodium were added in small portions at a time during a period of eight hours. The carbinol which crystallised out on cooling was recrystallised from amyl alcohol, and melted at 89·5°. It is much more soluble in ethyl alcohol than the ketone from which it is prepared.

The *acetate* prepared from the carbinol melted at 54—61°. Lack of sharpness in the melting point was observed by Kipping (Trans., 1890, **57**, 987) in the case of dipentadecylcarbinyl acetate prepared from palmitone, and the same phenomenon is noticed in the acetates of the carbinols obtained from cerotone and montanone:

0·1240 gave 0·3674 CO_2 and 0·1517 H_2O. C = 80·80; H = 13·54.

$C_{37}H_{74}O_2$ requires C = 80·73; H = 13·45 per cent.

Cerotone, $C_{51}H_{102}O$.

According to Beilstein (Vol. I., p. 1006), cerotone was obtained by Brückner by the distillation of lead cerotate, and melted at 62°, but the ketone prepared by Nafzger on distillation of the free acid melted at 92°. Mr. T. Rigg, M.Sc., kindly undertook the investigation of the action of iron turnings on cerotic acid, and supplies the following note.

The cerotic acid was prepared from beeswax by combining the methods of Brodie and of Marie, and melted at 77·5° (uncorr.).

Nine grams of the acid were heated with 0·69 gram of sifted cast-iron turnings, the temperature being allowed to rise to 350°, at which temperature the mixture was maintained for four hours. Evolution of carbon dioxide began at about 280°. After removal of iron and unchanged cerotic acid, the product of the reaction was recrystallised from light petroleum (b. p. 80—100°) until the melting point was constant. The yield was 55 per cent.; in a second experiment, in which the temperature was maintained at 360° for three hours, a 70 per cent. yield was obtained.

Cerotone prepared in this way melts at 93°; it is moderately soluble in light petroleum or ethyl acetate. It separates from hot glacial acetic acid in feathery groups of crystals. In hot ethyl alcohol it is almost insoluble, the solution merely becoming slightly turbid on cooling. (Found, C=83·50; H=13·93. Calc., C=83·80; H=13·97 per cent.)

Dipentecosylcarbinol, $(C_{25}H_{51})_2CH\cdot OH$, prepared by reducing cerotone with sodium in boiling amyl-alcoholic solution, melted at 95°. The *acetate* prepared from this alcohol melted at 58—60°:

0·1068 gave 0·3207 CO_2 and 0·1315 H_2O. C=81·89; H=13·67.

$C_{53}H_{106}O_2$ requires C=82·17; H=13·69 per cent.

Cerotoneoxime, $(C_{25}H_{51})_2C\colon NOH$, was prepared by boiling 1 gram of cerotone dissolved in 150 c.c. of amyl alcohol with 2 grams of hydroxylamine hydrochloride and excess of potassium hydroxide. It was crystallised from ethyl acetate, and melted at 78°:

0·1227 gave 0·3696 CO_2 and 0·1505 H_2O. C=82·15; H=13·61.

0·44 „ NH_3 equivalent to 4·95 c.c. $N/10$-HCl. N=1·58.

$C_{51}H_{103}ON$ requires C=82·14; H=13·82; N=1·87 per cent.

Montanone, $(C_{27}H_{55})_2CO$.

Montanic acid, prepared from Montan wax, was recrystallised from alcohol, and finally from glacial acetic acid until the melting point was constant at 82·5° (uncorr.). The titration value of the acid agreed sharply with that required for an acid of the formula $C_{28}H_{56}O_2$, as stated by Ryan and Dillon (*Sci. Proc. Roy. Dubl. Soc.*, 1909, **12**, 202), not with $C_{29}H_{58}O_2$, as given by Hell (*Zeitsch. angew. Chem.*, 1900, **14**, 556) and by Eisenreich (*Chem. Rev. Fett. Harz-Ind.*, 1909, **16**, 211).

The ketone was prepared as in the case of stearone, a 50 per cent. yield being obtained. It melts at 97°, and is conveniently recrystallised from glacial acetic acid:

0·1124 gave 0·3456 CO_2 and 0·1415 H_2O. C=83·85; H=13·98.

$C_{55}H_{110}O$ requires C=83·96; H=13·97 per cent.

Montanoneoxime melts at 82·5°, and is very sparingly soluble in alcohol, more readily so in ethyl acetate:

0·3371 gave NH_3 equal to 4·2 c.c. $N/10$-HCl. N = 1·74.
$C_{55}H_{111}ON$ requires N = 1·72 per cent.

The *alcohol* obtained by reduction of montanone melts at 101°; the corresponding *acetate* melts at 66°.

Melissone.

The melissic acid was prepared from New Zealand beeswax, and was separated from the cerotic acid by means of the very sparing solubility of sodium melissate in hot 95 per cent. alcohol, in which solvent sodium cerotate is rather easily soluble. The acid melted at 88·5° (uncorr.).

The ketone was prepared by heating the acid with metallic iron for two hours at 370°; the yield was 47 per cent. of that demanded by theory.

Melissone melts at 99·5°, is practically insoluble in boiling absolute alcohol, but may be conveniently recrystallised from amyl alcohol or glacial acetic acid:

0·0804 gave 0·2489 CO_2 and 0·1018 H_2O. C = 84·32; H = 14·06.
$C_{59}H_{118}O$ requires C = 84·08; H = 14·01 per cent.

Schwalbe (*Diss.*, Tübingen) observed a ketone melting at 97—99° amongst the products of the soda-lime fusion of myricyl alcohol from beeswax.

Melissoneoxime melts at 84°.

Oleone, $C_{35}H_{66}O$.

According to Beilstein (Vol. I., p. 1006) no ketones have hitherto been prepared from the unsaturated acids, $C_nH_{2n-2}O_2$. In Watt's Dictionary (Vol. IV., pp. 193 and 196) it is stated that Bussy obtained a neutral, oily liquid by distilling oleic acid with lime, and that he regarded this as oleone. Attempts to prepare oleone by the interaction of oleic acid and phosphoric oxide were unsuccessful, a viscid tar resulting, from which no definite compounds could be extracted by organic solvents. Oleone can, however, be isolated from the distillation products of barium oleate, and more readily from the reaction product of iron with oleic acid. It is also present in the fractions of highest boiling point of commercial oleic acid.

I.—Forty grams of barium oleate (Found, Ba = 19·4. Calc., Ba = 19·6 per cent.), recrystallised from a mixture of benzene and alcohol (Farnsteiner, *Zeitsch. Nahr. Genussm*, 1899, **2**, 1), were

heated in a flask immersed in a bath of molten solder. A slow current of hydrogen was passed into the flask throughout the operation, and the pressure was kept below 100 mm. A device similar to that used by Young (Trans., 1891, **59**, 623) was employed to remove the volatile products as rapidly as possible. A distillate first appeared at 280°/25 mm., and was pale yellow and mobile. As the temperature rose, the distillate became darker and more viscous, and the pressure in the apparatus rose. Distillation ceased, and the pressure again fell before a temperature of 450° was attained. The total distillate was a reddish-brown, viscous liquid showing a green fluorescence. A small quantity of crystals separated on keeping, and a further crop was obtained by fractionating the crude distillate under diminished pressure and cooling the fraction distilling between 280° and 330°/5—10 mm. The total weight of crystals was only 2 per cent. of that demanded by theory for the production of oleone from the barium salt.

After repeated crystallisation from alcohol the substance melted at 59°:

0·1062 gave 0·3252 CO_2 and 0·1260 H_2O. C = 83·3; H = 13·1.

By ebullioscopic method in alcohol: Found, M.W. = 492 and 508.

$C_{35}H_{66}O$ requires C = 83·66; H = 13·14 per cent. M.W. = 502.

The bromine absorption in chloroform solution after twelve hours was 62·1 per cent. The absorption of four atoms of bromine requires 63·8 per cent.

It is, of course, possible that in the formation of this oleone the position of the ethylene linkings may have changed from the positions occupied in the oleic acid.

It is not a little remarkable that the distillate boiling at 280—330°, from which the oleone crystals have been removed as far as possible by cooling and filtration, still has almost the same composition as the crystals themselves. (Found, C = 83·2; H = 13·0.) This calls to mind an observation by Miller and Tschitschkin (*Annalen*, 1899, **307**, 375) that the distillate from the calcium salt of azelaic acid yields a fraction boiling at 180—200°, the analysis of which agrees with that required for *cyclo*octanone; but the existence of this compound could only be proved in the fractions boiling above 200°.

II. *Preparation of Oleone by the Interaction of Iron and Oleic Acid.*—One gram of oleic acid prepared from the commercial acid by repeated rectification in a vacuum and removal of saturated fatty acids by freezing, and 5 grams of practically pure oleic acid (prepared from olive oil, solidifying completely at 14°, and yielding a lead salt completely soluble in ether) were separately heated with one-tenth of their weights of powdered and sifted cast-iron turnings.

Evolution of carbon dioxide began at 240°. The mixture was slowly heated to 340°, and this temperature maintained for two hours; much frothing occurred towards the end of the reaction. After removal of iron and acidic substances, the semi-solid product was crystallised several times from alcohol and acetic acid until the melting point was constant at 59·5°. The yield in each case was 10 per cent. of the oleic acid taken:

0·1089 gave 0·3335 CO_2 and 0·1332 H_2O. C=83·5; H=13·6.

$C_{35}H_{66}O$ requires C=83·6; H=13·1 per cent.

From oleic acid heated to 340° for two hours in the absence of iron no oleone could be isolated.

III. *Isolation of Oleone from Commercial Oleic Acid.*—Since commercial olein is prepared by the steam distillation of crude stearin from cast-iron retorts, the temperature in which frequently exceeds 300°, the presence of oleone is to be expected in commercial oleic acid. By the kindness of the directors and manager (Mr. Bull) of the New Zealand Candle Co. we have been supplied with samples taken during the redistillation of 2 tons of commercial olein, an operation extending over five hours.

The fractions collected during the first four hours distilled almost completely below 270°/50 mm. The portions passing over during the last fifteen minutes were filtered from solids, and only began to boil at 270°/50 mm.; a large portion boiled above 300°/25 mm.

Oleone was obtained from these higher fractions by dissolving in a large volume of alcohol and neutralising with sodium hydroxide, which caused the separation of an oil insoluble in the soap solution. This oil on keeping deposited crystals, which melted at 59° after repeated crystallisation from alcohol and acetic acid.

When prepared by any of these methods *oleone* is a colourless substance, crystallising from alcohol or acetic acid in hair-like needles. It is sparingly soluble, even in boiling alcohol, more readily so in ether, ethyl acetate, glacial acetic acid, or chloroform.

Oleoneoxime melts at 31°, and is readily soluble in alcohol:

0·1334 gave 2·9 c.c. N_2 at N.T.P. N=2·73.

$C_{35}H_{67}ON$ requires N=2·70 per cent.

Reduction of Oleone to Pentatriacontane.—0·5 Gram of oleone was warmed with phosphorus pentachloride, and the product subsequently reduced with hydriodic acid and phosphorus at 240°. The resulting hydrocarbon was recrystallised from ether, and melted at 73°. (Found, C=85·8; H=14·8. Calc., C=85·3; H=14·6 per cent.) Pentatriacontane melts at 74·7° (Krafft, *Ber.*, 1882, **15**, 1715).

Elaidone.

Two grams of pure elaidic acid were heated with iron under similar conditions to those employed for the preparation of oleone. The elaidone was recrystallised from alcohol, and melted at 70°. The yield was only 15 per cent. when the maximum temperature employed was 320°; a larger yield was obtained in an experiment in which the maximum temperature was 350°, but the ketone produced at the higher temperature was not readily brought to a sharp melting point by recrystallisation:

Found: C=83·33; H=13·27.

$C_{35}H_{66}O$ requires C=83·62; H=13·14 per cent.

Elaidoneoxime crystallises from alcohol in long needles, which melt at 32°; it is more readily soluble than the oxime of oleone:

0·3678 gave NH_3 equal to 7·8 c.c. *N*/10-HCl. N=2·96.

$C_{35}H_{67}ON$ requires N=2·71 per cent.

Brassidone.

This was prepared from brassidic acid and metallic iron, and melts at 80°. The yield at 280° was 20 per cent., at 320° 50 per cent., of the acid employed. The compound is readily soluble in hot alcohol:

0·1237 gave 0·3787 CO_2 and 0·1495 H_2O. C=83·42; H=13·42.

$C_{43}H_{82}O$ requires C=84·03; H=13·33 per cent.

Brassidoneoxime melts at 51°:

0·3078 gave NH_3 equal to 4·6 c.c. *N*/10-HCl. N=2·19.

$C_{43}H_{83}ON$ requires N=2·22 per cent.

Action of Iron on Erucic Acid.

Carefully purified eruric acid was heated with powdered iron turnings for three hours at 300—320°. The resulting neutral compound, even after repeated recrystallisation from a variety of solvents, melted at 50—60°, although the analytical numbers agreed with those required for erucicone. (Found, C=83·88; H=13·54. $C_{43}H_{82}O$ requires C=84·04; H=13·33 per cent.) From the products of distillation of barium erucate under diminished pressure a similar product of indefinite melting point was obtained.

The result would be readily explained if, during the process of heating, a portion of the erucic acid were changed into any of the numerous possible isomerides, so that the ultimate product would be a mixture of isomeric ketones.

Some support in favour of this view is given by the observation

that a sample of the same erucic acid when heated alone for two hours at 280—300° yielded a small quantity of an acid melting at about 50°. The original erucic acid melted at 34°.

The expenses of this investigation have been defrayed by a grant from the Research Scholarship Fund of the Government of New Zealand.

Victoria College,
Wellington, N.Z.

CCLIV.—*The Separation of Mixtures of Organic Acids by Partial Esterification.*

By John Joseph Sudborough and Ebenezer Rees Thomas.

The difference between the esterification constant of an $\alpha\beta$-unsaturated acid and its saturated analogue, and between the constants of corresponding $\alpha\beta$- and $\beta\gamma$-acids, and also $\alpha\beta$- and $\gamma\delta$-acids (Trans., 1905, **87**, 1840; 1907, **91**, 1033; 1909, **95**, 315, 975), suggested that possibly mixtures of those acids might be separated by partial esterification. It was found that under specific conditions a separation is brought about by one treatment with alcohol and hydrogen chloride, that the method is perfectly general, and that it can be used whether the composition of the mixture is known or not.

For any such mixture of acids the following general method may be used. The mixture is treated with $0 \cdot 22N$-ethyl-alcoholic hydrogen chloride, when the more readily esterified acid has $E^{15°}_{MeOH}$ about 40. When it is less, the strength of the hydrogen chloride must be rather more than $0 \cdot 22 \times 40 \times N/E'$ (where E' is the esterification constant of the more readily esterified acid in the mixture). About twenty-five to thirty times the amount of alcohol required to combine with the weight of the more readily esterified acid present must be taken. When the composition of the mixture is unknown, it may be regarded as all more readily esterifiable acid. The solution is left at about 20° for five hours or longer,* and then poured into

* With acids of $E^{15°}_{MeOH}$ about 80 a shorter time will suffice. In all cases if left considerably longer than the exact time required, very little difference will be made. In one experiment where four and a-half hours would have been a suitable period, the mixture was left for seventeen and a-half hours and a good separation was obtained (Expt. 1).

about four times its volume of water; the liquid is made slightly alkaline with sodium carbonate, the ester extracted with ether, the extract washed, dried, and distilled, and the ester hydrolysed. The acid may be obtained either by acidifying the alkaline liquid and extracting with ether, or, where insoluble in water, by precipitation. In some cases it may be convenient to obtain the greater part by precipitation, the remainder being extracted from the filtrate with ether.

In working out the conditions, preliminary experiments were carried out, 1 c.c. of the solution being titrated from time to time with standard alkali. Where the $E^{15^\circ}_{MeOH}$ of the acids present in the mixture is unknown, the conditions may be found in this way.

The method has been used for:

A. *Separation of αβ-Unsaturated Acids from their Saturated Analogues.*

i. *Cinnamic and β-Phenylpropionic Acids* (compare experiments 1—6).—The method is of interest in this case in view of the fact that in the preparation of β-phenylpropionic acid by the reduction of cinnamic acid, the reduction is seldom complete, and the resulting product is somewhat difficult to purify by recrystallisation.

ii. *Crotonic and Butyric Acids* (compare experiments 7 and 8).

iii. *Dimethylacrylic and* iso*Valeric Acids* (compare experiments 9 and 10).

B. *Separation of Mixtures of αβ- and βγ-Unsaturated Acids.*

The method is of interest in two special cases:

i. Where, as in the case of β-ethylacrylic and ethylidenepropionic acids, a mixture of the acids is produced during their preparation. (For separation see experiments 13 and 14.)

ii. When a mixture of the two acids is obtained by boiling the βγ-acid for twenty to fifty hours with excess of sodium hydroxide (Fittig, *Annalen*, 1894, **283**, 51), for example, hydrosorbic and αβ-hexenoic acids. (For separation see experiments 15 and 16.)

A mixture of cinnamic acid and phenyl*iso*crotonic acid was also separated by this method (compare experiments 11 and 12).

The method at present in use for the separation of αβ- and βγ-unsaturated acids is that described by Fittig (*loc. cit.*). With this method (i) considerable difficulty is experienced in working it. Fittig states (*loc. cit.*), "dass sie in anderen Händen nicht immer zu so glatten Resultaten geführt hat." Several experiments on the purification of αβ-pentenoic acid by Fittig's method were carried

out by the authors (Trans., 1907, **91**, 1035), and in these cases very poor yields were obtained, although great care was taken as to conditions. The method here described presents none of these difficulties, and one esterification is sufficient to give a good separation, whilst three treatments with sulphuric acid are necessary in order to obtain the $\alpha\beta$-acid pure.

(ii) All the $\beta\gamma$-acid is lost in the form of the γ-lactone. In the case of hydrosorbic acid, the yield of crude $\alpha\beta$-acid is never more than 30 per cent. of the weight of hydrosorbic acid used (*Annalen*, 1894, **283**, 119), 70 per cent. being thus practically destroyed. In the partial esterification method the only appreciable loss is due to the inevitable formation of hydroxy-acid—about 25 per cent. of the weight of hydrosorbic acid used.

(iii) It has been shown by Fichter (*Ber.*, 1909, **42**, 4707) that β-methyl-Δ^{α}-pentenoic acid is quantitatively transformed into lactone under the conditions described by Fittig for the purification of $\alpha\beta$-acids. They were therefore unable to determine whether β-methyl-Δ^{β}-pentenoic acid was transformed into the Δ^{α}-acid or not by boiling with sodium hydroxide solution. It is hoped that the method described in this paper may be of some use in deciding this point.

C. *Separation of $\alpha\beta$- and $\gamma\delta$-Acids.*

A mixture of δ-phenyl-Δ^{α}- and Δ^{γ}-pentenoic acids was separated in this way (compare experiment 17).

EXPERIMENTAL.

Experiment 1.—*Cinnamic and β-Phenylpropionic Acids* (preliminary).—Two grams of cinnamic acid (recrystallised storax acid) and 2·5 grams of β-phenylpropionic acid (m. p. 47·5°) were dissolved in 15 c.c. of ethyl alcohol, and 5 c.c. of 0·89N-solution of hydrogen chloride in ethyl alcohol added, thus giving 20 c.c. of 0·22N-hydrogen chloride. In order to watch the course of the reaction, 1 c.c. was removed from time to time, and titrated with 0·0262N-barium hydroxide solution, of which by calculation hydrogen chloride required 8·5 c.c.; cinnamic acid, 25·5 c.c.; together 33·5 c.c.; β-phenylpropionic acid, 31 c.c.

After	0·3	0·5	1	1·5	2·5	4	17·5	hours
1 c.c. required	50	48	43·7	40	36	33·7	28	c.c.

From these results it was concluded that presumably nearly all the β-phenylpropionic acid was esterified at the end of about four hours under these conditions, whilst even after leaving for another thirteen hours, only a comparatively small quantity of the cinnamic

acid was esterified. To test this conclusion, the remainder of the alcoholic solution (which had been left for 17·5 hours) was poured into water, and treated as described in the introduction.

1·20 Grams of an acid, melting at about 131°, and 2·08 grams of an ester were obtained. The ester, when hydrolysed, yielded 1·64 grams of an acid melting at 45—47°.

Experiment 2.—*Cinnamic and β-Phenylpropionic Acids.*—A mixture of 10 grams of each acid was dissolved in 75 c.c. of ethyl alcohol, and 25 c.c. of 0·89*N*-hydrogen chloride in alcohol added. The mixture was left at 18° for about five hours, then poured into 400 c.c. of water, and treated as described in the introduction.

11·99 Grams of ester were obtained, and from the alkaline liquid, after rendering acid and extracting with ether, 9·56 grams of cinnamic acid (m. p. 129·5—132°) were obtained.

The ester was distilled, and 11·20 grams, boiling at 244—246°/772 mm., were collected. This was hydrolysed by means of sodium hydroxide solution, and the acid recovered as before.

8·96 Grams of β-phenylpropionic acid (m. p. 46—47·5°) were obtained. 5·72 Grams of this acid were pressed on filter-paper, and then melted at 48—49°. The melting point given by Fock (*Ber.*, 1890, **23**, 148) is 48·7°. Hence 4·5 grams of this acid were recrystallised from light petroleum (b. p. 35—42°). Three fractions were obtained; (i) 2·73 grams, m. p. 48·5—49·5°; (ii) 1·0 gram, m. p. 48—49°; (iii) 0·76 gram, m. p. 47—48°.

An experiment was subsequently carried out with a mixture (in equal proportions) of these acids, the cinnamic acid being recovered by precipitation.

Experiment 3.—Five grams of each acid were dissolved in 40 c.c. of ethyl alcohol, 10 c.c. of 1·08*N*-hydrogen chloride in ethyl alcohol were added, and the solution left at 20° for six hours. The mixture was then poured into water, and the ester extracted as before; 5·57 grams of ester, boiling at 243—245°/758 mm., were obtained (=4·83 grams of acid).

The alkaline solution was carefully heated on the steam-bath so as to remove all the ether, cooled, and treated with concentrated hydrochloric acid in excess, when 4·73 grams of cinnamic acid (m. p. 129—131°) were obtained.

Experiments were then conducted to study the conditions for separation when the two acids are not present in equal proportions.

A. *When β-Phenylpropionic Acid is in the Larger Proportion.*

Experiment 4.—Three grams of β-phenylpropionic acid and 1 gram of cinnamic acid were dissolved in 15 c.c. of alcohol, 5 c.c. of 0·89*N*-hydrogen chloride added, and 1 c.c. of the solution

titrated from time to time with 0·0262*N*-barium hydroxide solution, of which by calculation hydrogen chloride requires 8·5 c.c.; cinnamic acid, 12·75 c.c.; together 21·2 c.c.; β-phenylpropionic acid, 43·75 c.c.:

After	1	2	4	5·5	hours
1 c.c. required	32·6	28·3	23·4	22·2	c.c.

The mixture was left for another hour (6·5 hours in all), and then poured into water and treated as before, giving 0·94 gram of cinnamic acid (m. p. 127—129°) and 2·55 grams of β-phenylpropionic acid, which, on pressing on filter-paper, lost a little oil and melted at 48·8—49·4°.

B. *When Cinnamic Acid is in the Larger Proportion.*

Experiment 5.—Three grams of cinnamic acid and 1 gram of β-phenylpropionic acid were dissolved in 15 c.c. of alcohol (solution warmed and cooled), and 5 c.c. of 0·89*N*-alcoholic hydrogen chloride added. One c.c. was removed and titrated as before with 0·0262*N*-barium hydroxide solution, of which hydrogen chloride required 8·5 c.c.; cinnamic acid, 38·0 c.c.; together 46·5 c.c.; β-phenylpropionic acid, 12·6 c.c. After one and 1·5 hours, 1 c.c. required 44·3 and 43·7 c.c. respectively.

At the end of 1·5 hours, the mixture was poured into water and treated as before, and 0·97 gram of ester and 2·72 grams of cinnamic acid (m. p. 126—128·5°) were obtained.

Experiment 6.—*Purification of crude β-phenylpropionic acid, which had been prepared by the reduction of cinnamic acid.*—The crude acid (10·2 grams, m. p. 41—45°) was shaken with alcohol (84 c.c.), and, after settling, the clear liquid was decanted. The flask was rinsed with 10 c.c. of alcohol, which was filtered and added to the solution (weight of insoluble residue = 0·10 gram). 1·08*N*-Alcoholic hydrogen chloride (25 c.c.) was then added, and the mixture left at 20° for about nine hours. It was poured into water, and treated as before. The ester was distilled, and 10·2 grams of ester (b. p. 243—246°/758 mm.) were obtained (= 8·5 grams of acid).

The acid impurity was precipitated from the solution of the sodium salt with hydrochloric acid, collected, washed with water, and dried, when 1·30 grams of cinnamic acid (m. p. 128·5—130°) were obtained.

Separation of Crotonic and Butyric Acid.

Crotonic acid ($E^{15°}_{MeOH}$ = 1·28), melting at 71—71·4°, and butyric acid ($E^{15°}_{MeOH}$ = 41·63), boiling at 164—165°, were used.

Experiment 7 (preliminary).—A mixture of 2 grams of each acid was dissolved in 15 c.c. of alcohol, and 5 c.c. of 0·89*N*-alcoholic hydrogen chloride were added. 1 C.c. of the mixture was titrated with 0·0262*N*-barium hydroxide solution, of which hydrogen chloride requires 8·5 c.c.; crotonic acid, 45·0 c.c.; together 53·5 c.c.; butyric acid, 44 c.c. After 1, 2, and 4·5 hours, 1 c.c. required 65, 60, and 51·6 c.c. respectively.

At the end of 4·5 hours the mixture was poured into water, and treated as before. 1·69 Grams of crotonic acid (m. p. 65—69°) were obtained. Owing to its extreme volatility, no constant weight of the ester could be observed. The conditions for the separation of these two acids are therefore exactly similar to those used for cinnamic and β-phenylpropionic acids, except that precautions must be taken to avoid loss of ester by volatilisation.

Experiment 8.—Ten grams of each acid were mixed and dissolved in 80 c.c. of alcohol, and 21 c.c. of 1·08*N*-alcoholic hydrogen chloride were added. The mixture was left at 18° for nearly four and a-half hours, poured into water, and neutralised as before; it was then extracted three times with ether, and the ethereal extract washed three times with one-third its volume of water, and dried. The acid was obtained in a similar manner on acidifying with hydrochloric acid and extracting with ether.

To avoid loss of ethyl butyrate by volatilisation with the ether vapour, the residue was distilled very slowly from a small distillation flask with a comparatively long neck. A constriction was made at the lower end of the neck, which was filled with glass beads, and a tube for the introduction of more of the liquid passed through the beads and was closed by rubber and a pinchcock at the upper end. Ten grams of ethyl butyrate (b. p. 120—121°/773 mm.) were obtained.

The crotonic acid was distilled and left in a desiccator. 8·98 Grams of acid, melting at about 61°, were obtained. 2·6 Grams were recrystallised from light petroleum (b. p. 40—60°), and gave 1 gram melting at 71—71·2°, 0·9 gram melting at 69·5—70°, and 0·45 gram melting at 67—69°.

Separation of Dimethylacrylic and iso*Valeric Acids.*

Dimethylacrylic acid ($E^{15^\circ}_{MeOH} = 0·285$, m. p. 67·8—68°), prepared by Barbier and Leser's method (*Bull Soc. chim.*, 1905, [iii], **33**, 815) from mesityl oxide and sodium hypochlorite, and *iso*valeric acid ($E^{15^\circ}_{MeOH} = 12·3$, b. p. 174·5—175·1°/740 mm.) were used in the experiment.

Experiment 9 (preliminary).—As the esterification constants of these acids are approximately one-quarter of those of cinnamic and

β-phenylpropionic acids, it was thought advisable to use alcoholic hydrogen chloride four times as strong as that used in the previous experiments, the rate of esterification being proportional to the strength of the hydrogen chloride. Hence a mixture of 2 grams of dimethylacrylic acid and 2·3 grams of *iso*valeric acid was dissolved in 10 c.c. of alcohol, and 15 c.c. of 1·46*N*-alcoholic hydrogen chloride were added. One c.c. of this solution was titrated against 0·031*N*-barium hydroxide solution, of which hydrogen chloride required 28·2 c.c.; dimethylacrylic acid, 25·3 c.c.; together 53·5 c.c.; *iso*valeric acid, 29·1 c.c. After leaving for four and six and a-half hours, 1 c.c. required 57·1 and 53·7 c.c. respectively, thus under these conditions leaving for six and a-half hours will probably bring about a separation.

Experiment 10.—Ten grams of dimethylacrylic acid were dissolved on warming in 20 c.c. of alcohol. The solution was cooled, and 10 grams of *iso*valeric acid were added. To the solution 90 c.c. of 1·08*N*-alcoholic hydrogen chloride were added, and the mixture was left at 20° for six and a-half hours. It was then poured into water and treated as before. The ether was in this case also distilled off very carefully from the ester, and the following fractions were collected: Below 78°; 78—100°; and, of which 9·65 grams were obtained, 133—135°/737 mm. Ether was added to the fraction b. p. 78—100°, which was then treated twice with its own volume of water, the ethereal layer being separated and dried. The fraction b. p. 133—135°/740 mm., obtained on distillation, was added to the former amount of ester obtained; the total weight of pure ester was 11·23 grams. As dimethylacrylic acid is appreciably soluble in water, the solution of the sodium salt was evaporated to a small volume, cooled, and then acidified with hydrochloric acid. The weight of acid obtained was 6·10 grams (m. p. 67·3°), and from the aqueous filtrate was extracted, by means of ether, 3·45 grams, of which 2·12 grams were pressed on a porous plate, yielding 1·90 grams of acid melting at 69°.

Separation of Mixtures of αβ- and βγ-Unsaturated Acids.

*Cinnamic Acid and Phenyl*iso*crotonic Acid* ($E^{15°}_{MeOH} = 86·6$).—Recrystallised storax cinnamic acid and phenyl*iso*crotonic acid (m. p. 86°), prepared from phenylparaconic acid (Trans., 1907, **91**, 1034), were used.

Experiment 11.—A mixture of 2 grams of each acid was dissolved in 20 c.c. of warm alcohol, and the solution cooled; 5 c.c. of 1·08*N*-alcoholic hydrogen chloride were added, and 1 c.c. of the mixture titrated as before with 0·0262*N*-barium hydroxide

solution, of which hydrogen chloride required 8·2 c.c.; cinnamic acid, 20·6 c.c.; together 28·8 c.c.; phenyl*iso*crotonic acid, 18·8 c.c. After 2·6 hours, 1 c.c. required 27·0 c.c. of the alkali, and the mixture was then poured into water and treated as before: 2·25 grams of ethyl phenyl*iso*crotonate were obtained, yielding on hydrolysis 1·81 grams of acid (m. p. 76—79°) and 2·21 grams of cinnamic acid (m. p. 124—127°). Hence for such a mixture under these conditions three hours is probably sufficient.

Experiment 12.—Ten grams of each acid were mixed and dissolved in 80 c.c. of alcohol, and 21 c.c. of 1·08*N*-alcoholic hydrogen chloride added. The mixture was left at 20° for three hours, and then poured into water and treated as before. On evaporation of the ether, 10·53 grams of an acid, melting at 125—127°, were obtained, and a faint odour of benzaldehyde was noticed. 10·4 Grams of this acid were neutralised with sodium carbonate solution, and the solution was boiled until the odour of benzaldehyde was no longer perceptible. On acidifying with hydrochloric acid, about 9·2 grams of acid, melting at 131—133°, were obtained.

After removal of ether, the ester was carefully distilled under the ordinary pressure, and 9 grams of a fraction boiling at 281—282°/763 mm. were collected. A further 1·6 grams passed over about this temperature, the small amount of liquid making it difficult to read the temperature accurately. The mercury finally rose to 290°, when the distillation was stopped. Slight decomposition takes place during the distillation, a little tarry residue being left in the flask.

This ester does not appear to have been described, hence its composition was determined:

0·3182 gave 0·8880 CO_2 and 0·2088 H_2O. C = 76·1; H = 7·30.
0·2486 „ 0·6954 CO_2 „ 0·1686 H_2O. C = 76·2; H = 7·53.

$C_{12}H_{14}O_2$ requires C = 75·8; H = 7·37 per cent.

The *ethyl phenyl*iso*crotonate* obtained in this way had D^{20} 1·030.

β-Ethylacrylic and Ethylidenepropionic Acids.

The mixture of these acids was prepared as before (Trans., 1907, **91**, 1035).

Experiment 13.—From 50 grams of malonic acid, 16 grams of the fraction boiling at 190—205°/756 mm. were collected. This was left in a desiccator overnight, and then tested by titrating a known weight with standard alkali:

0·0976 required 30 c.c. 0·0262*N*-barium hydroxide. Calc., 37·3 c.c.
0·1330 „ 40·65 c.c. „ „ Calc., 50·8 c.c.

Hence this liquid probably contains as impurity some neutral sub-

stance in addition to the two acids. It was purified as follows: The liquid was shaken with a solution of sodium carbonate, and extracted three times with ether, the ethereal solution finally yielding 3 grams of a neutral oil boiling at about 200°.

The alkaline solution was acidified with hydrochloric acid, and extracted with ether as before; 10·5 grams of a fraction boiling at 190—203° were obtained:

0·0682 required 26·05 c.c. 0·0262*N*-barium hydroxide. Calc., 26·0 c.c.

Hence probably a mixture of β-ethylacrylic and ethylidenepropionic acids was present.

Separation of the Mixture.—Ten grams of the mixture were placed in a flask, and 60 c.c. of alcohol and 15 c.c. of 1·08*N*-alcoholic hydrogen chloride were added. The solution was left at 20° for four and a-half hours, and then poured into water and treated as before. The ether was very slowly distilled from the ethereal solution of the acid, using the glass beads, etc., described in experiment 8.

4·7 Grams of acid, boiling at about 200°, were obtained. Some ether was distilled off from the ethereal solution of the ester, and the remainder kept for treatment with that obtained in experiment 14.

Experiment 14.—The mixture of acids was prepared as before, 16 grams of a fraction boiling at 190—205° being obtained. This was purified as described in experiment 13, and 9·3 grams of acid boiling at 190—203° were obtained:

0·1496 required 55·5 c.c. 0·0262*N*-barium hydroxide. Calc., 57 c.c.
0·0932 „ 34·3 c.c. „ „ Calc., 35·5 c.c.

The mixture therefore contained only 97 per cent. of the acids.

Separation of the Mixture.—Nine grams of the mixture were mixed with 60 c.c. of alcohol, 17 c.c. of 1·08*N*-alcoholic hydrogen chloride added, and the solution left at 20° for four and a-half hours. It was then poured into water, and treated exactly as in experiment 13. 4·35 Grams of acid, boiling at 198—201°/737 mm. were obtained, and this was added to the 4·7 grams obtained in experiment 13. The mixture, on distillation, gave 8·3 grams of ethylacrylic acid (b. p. 197—201°/751 mm.). This was placed in a freezing mixture, when the greater part solidified, melting at 5° (Fittig and Mackenzie, *Annalen*, 1894, **283**, 83, give 9·5—10·5° as the melting point of the pure acid).

The ethereal solution of the ester was mixed with that obtained in experiment 13, and the ether slowly distilled, using a rod-and-disk fractionating column. When nearly all the ether had been

removed, the ester was hydrolysed by means of barium hydroxide solution, and the crystalline barium ethylidenepropionate obtained and weighed.

Four hundred c.c. of barium hydroxide solution (saturated at 15°) were added to the ester, and the whole was boiled in a reflux apparatus for two hours, when apparently complete hydrolysis had taken place. The liquid was extracted once with ether to remove any unhydrolysed ester, and then freed from ether by passing steam through it. Carefully washed carbon dioxide was then passed through the hot solution to precipitate any excess of barium hydroxide, and the solution filtered. On evaporating to a small volume, cooling, and adding alcohol, pearly-white crystals were precipitated. These were removed, washed with alcohol, pressed on a porous plate, and dried in the steam-oven. Weight = 5·7 grams.

The solution and washings were evaporated to dryness, and the crystals obtained were treated in the same way as the former fraction: 5·8 grams were obtained, making a total of 11·5 grams of barium ethylidenepropionate (7 grams of acid). As the barium salt of ethylacrylic acid is a gum, the former salt must be almost pure, and, by one esterification, it has been possible to obtain 8·3 grams of pure ethylacrylic acid and 7 grams of pure ethylidenepropionic acid from 19 grams of the mixture.

Transformation of Hydrosorbic Acid into αβ-Hexenoic Acid and Purification of the Mixture Obtained by Partial Esterification.

Hydrosorbic acid was prepared as described by Sudborough and Thomas (Trans., 1910, **97**, 2450) by the reduction of sorbic acid in alkaline solution by means of 3 per cent. sodium amalgam. 13·7 Grams of the acid were treated as described by Fittig (*Annalen*, 1894, **283**, 117) with 266 c.c. of 20 per cent. sodium hydroxide solution, the solution being boiled under a reflux condenser for thirty-five hours: 10·27 grams of a yellow oil, presumably a mixture of αβ-hexenoic and hydrosorbic acids, were obtained by steam distillation, and 3·1 grams of hydroxy-acid from the residue. The αβ-hexenoic and hydrosorbic acids were separated as follows.

Experiment 15.—10·27 Grams of the mixture were treated with 60 c.c. of alcohol and 20 c.c. of 1·02*N*-alcoholic hydrogen chloride, and left for five and a-half hours at 20°. The mixture was then separated by exactly the same method as that adopted in the previous experiments, the ester being very carefully freed from ether. Nine grams of ester, boiling at 170—172°/762 mm., were obtained. The aqueous solution was heated on a steam-bath to

remove ether and alcohol, and then evaporated to a small volume. On cooling, the $\alpha\beta$-hexenoic acid was precipitated by addition of hydrochloric acid in excess, when 0·9 gram was obtained, which melted at 32·1—32·3° (Fittig gives 32·7—33·1° as the melting point of the pure acid). The aqueous filtrate was extracted three times with ether, the ethereal extract yielding 1·7 grams of acid, nearly all of which solidified—a trace of oil being observed.

Experiment 16.—The 9·0 grams of ester were first carefully hydrolysed and then boiled with sodium hydroxide as before for thirty-five hours. 5·83 Grams of the mixture of $\alpha\beta$-hexenoic and hydrosorbic acids were obtained, and to this 34 c.c. of alcohol and 14 c.c. of 0·947*N*-alcoholic hydrogen chloride were added, and the solution left for five and a-half hours. It was then poured into water, and treated as before, except that, the acid being only a small quantity, the solution of the sodium salt was evaporated so as to precipitate all the acid. 5·55 Grams of ester (b. p. 170—172°) and 0·4 gram of acid (m. p. 27·5—28·5°) were obtained.

Separation of $\alpha\beta$- and $\gamma\delta$-Unsaturated Acids.

$\alpha\delta$-Hydrocinnamylidenemalonic acid,

$$CH_2Ph{\cdot}CH{:}CH{\cdot}CH(CO_2H)_2,$$

was prepared as described by Riiber (*Ber.*, 1904, **37**, 2274; compare also Trans., 1910, **97**, 2452).

To obtain the corresponding substituted acetic acid, this acid was boiled with water, as described by Riiber (*Ber.*, 1905, **38**, 2746). The oily δ-phenyl-Δ^{β}-pentenoic acid obtained did not crystallise from light petroleum as stated by Riiber, and gave 188 as the mean of two determinations of its equivalent weight (δ-phenyl-Δ^{β}-pentenoic acid = 176, corresponding hydroxy-acid = 194). Apparently there was some hydroxy-acid present. The oil was, however, without further purification used for treatment with sodium hydroxide solution, as described by Riiber, for conversion into a mixture of the isomeric $\alpha\beta$-, $\beta\gamma$-, and $\gamma\delta$-acids with some hydroxy-acids; 13·2 grams of such a mixture were obtained, giving 4·1 grams of insoluble hydroxy-acid (m. p. 129—130°) and 8·7 grams of a mixture of $\alpha\beta$-, $\beta\gamma$, and $\gamma\delta$-acids on treatment with boiling carbon disulphide.

The mixture of unsaturated acids was pressed on a porous plate, the oily $\beta\gamma$-acid being absorbed, and 5·5 grams of a mixture of $\alpha\beta$- and $\gamma\delta$-acids obtained. This was dried in a desiccator, and separated as follows.

Experiment 17.—Thirty-six c.c. of alcohol and 12 c.c. of 0·947*N*-alcoholic hydrogen chloride were added to the 5·5 grams

of the mixture, the solution left for five and a-half hours at 20°, and then poured into water and treated as before, 4·03 grams of ester being obtained.

The alkaline aqueous solution was evaporated to a small volume, acidified with hydrochloric acid, the precipitated acid removed, and the filtrate extracted with ether: 1·75 grams of the *αβ*-acid (m. p. 99—101°; Riiber gives 104°) were obtained by precipitation, whilst 0·12 gram remained in the flask after removal of ether from the ethereal extract.

The 4·03 grams of ester were hydrolysed, and the acid recovered in exactly the same way as that used for the *αβ*-acid: 3·15 grams of acid (m. p. 79—82°; Sudborough and Thomas give 91°) were obtained by precipitation, and 0·4 gram from the ethereal extract. The latter contained a little oil, and when pressed on a porous plate melted at 126—128°; it was therefore probably the hydroxy-acid.

2·9 Grams of the acid (m. p. 79—82°) were recrystallised from light petroleum (b. p. 60—80°), a small quantity of insoluble matter being removed, and 1·75 grams of crystals, melting at 88—89°, and 0·85 gram, melting at 84—86°, were obtained.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH.

CCLV.—*The Absorption Spectra of Various Iodine Derivatives of Benzene and Toluene as Vapours, in Solution, and in Thin Films.*

By JOHN EDWARD PURVIS.

THE author has previously given accounts of investigations of the ultraviolet absorption spectra of the vapours of chloro- and bromobenzene, of *o*- and *m*-dichloro- and dibromo-benzene, and of *o*- and *m*-chloro- and bromo-toluene (this vol., pp. 811 and 1699).

The investigation has been continued with iodobenzene, *o*- and *m*-iodotoluene, and *o*- and *m*-di-iodobenzene. The apparatus employed and the general experimental method have been described before (*loc. cit.*).

Vapours.—Iodobenzene.

TABLE I.

The absorption spectrum of iodobenzene in a 1-dcm. tube has been studied by Pauer (*Ann. Phys. Chem.*, 1897, [iii], **61**, 363),

who observed two bands at λ 2625 and λ 2620. The author has studied the vapour of the substance at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. No such bands were observed, and the following table describes the absorption under the varying conditions of temperature and pressure

t°.	Pressure in mm.	
19°	767	The rays were transmitted to the Cd line 2313, which was fairly strong
30	811	The rays were transmitted to the Cd line 2329; the Cd lines 2321 and 2313 were just visible
45	837	The rays were transmitted to about λ 2630, where they gradually faded away; the Cd line 2573 was weak, and the rays were then feebly transmitted from about λ 2500 to about λ 2350, where they were again absorbed.
60	867	The rays were transmitted to about λ 2700
75	897	The rays were transmitted to about λ 2850; the Cd line 2748 was just visible
90	927	The rays were transmitted to about λ 2930, and the Cd line 2881 was just visible

A careful search was made for the two bands described by Pauer, but none were found. The vapour showed no absorption bands at any of the temperatures and pressures employed, whereas a considerable number of absorption bands were found in the vapours of the corresponding chlorine and bromine compounds (*loc. cit.*).

The absorption phenomena of the vapours of *o*- and *m*-iodotoluene were also studied in a column 200 mm. long and 20 mm. diameter, and no bands were observed. The following tables (II and III) describe the phenomena observed at various temperatures and pressures.

o-*Iodotoluene.*

Table II.

t°.	Pressure in mm.	
17°	766	The rays were transmitted to about λ 2300; the Cd line 2288 was just visible
30	810	The rays were transmitted to about λ 2310
45	836	The rays were transmitted to about λ 2340; the Cd lines 2329 and 2321 were just visible
60	866	The rays were transmitted to about λ 2400; they were very weak from about λ 2650 to λ 2500; the Cd line 2573 was not very strongly marked
75	896	The rays were transmitted to about λ 2800; the Cd line 2748 was very weak
90	926	The rays were transmitted to about λ 2900; the Cd line 2837 was just visible

m-*Iodotoluene.*

TABLE III.

$t°$.	Pressure in mm.	
17°	763	The rays were transmitted to about λ 2330; the Cd lines 2329, 2321, and 2313 were visible
30	807	The rays were transmitted to about λ 2330; the Cd lines 2329 and 2321 were visible
45	833	The rays were transmitted to about λ 2360
60	863	The rays were transmitted to about λ 2670; the Cd line 2573 was only moderately strong
75	893	The rays were transmitted to about λ 2830; the Cd line 2748 was only moderately strong
90	923	The rays were transmitted to about λ 2900; the Cd line 2837 was just visible

Like the vapour of *o*-iodotoluene, the vapour of *m*-iodotoluene exhibited no absorption bands at any of the above temperatures and pressures, whereas a considerable number of bands were found in the vapours of the corresponding chlorine and bromine compounds (*loc. cit.*).

As regards the vapours of the two solids *o*- and *m*-di-iodobenzene, the melting points of which are 27° and 40° respectively, each substance was introduced in the 200 mm. tube which was placed in the water-bath at 45°. Two series of experiments were taken, one under a constant diminished pressure and at various temperatures, and the other at varying pressures and temperatures. No bands were observed, and the tables IV, V, and VI describe the phenomena observed.

o-*Di-iodobenzene.*

TABLE IV.

The following table describes the phenomena observed in the vapour of *o*-di-iodobenzene at varying temperatures and constant pressure.

$t°$.	Pressure in mm.	
47	17	The rays were transmitted to λ 2250; the Cd lines 2239, 2194, and 2144 were visible
60	17	The rays were transmitted to λ 2250; the Cd lines 2239 and 2194 were visible
75	17	The rays were transmitted to about λ 2380; the Cd lines 2329 to 2265 were visible
90	17	The rays were transmitted to λ 2410; the Cd lines 2329 to 2265 were visible, but weaker than at 75°.

TABLE V.

The following table describes the phenomena observed in the vapour of *o*-di-iodobenzene at varying temperatures and pressures.

$t°$.	Pressure in mm.	
45	757	The rays were transmitted to about λ 2400 ; the Cd lines from 2329 to 2194 were visible
60	857	The rays were transmitted to λ 2550 ; the Cd lines 2329 to 2265 were very weak
75	887	The rays were transmitted to λ 2650 ; the Cd line 2573 was weak
90	917	The rays were transmitted to λ 2850 ; the Cd line 2748 was weak

m-*Di-iodobenzene.*

TABLE VI.

The following table describes the phenomena observed in the vapour of *m*-di-iodobenzene at varying temperatures and pressures.

$t°$.	Pressure in mm.	
45°	757	The rays were transmitted to λ 2240 ; the Cd lines 2194 and 2144 were visible
60	857	The rays were transmitted to λ 2450 ; the Cd lines 2329 to 2265 were weak
75	887	The rays were transmitted to λ 2550
90	917	The rays were transmitted to λ 2650 ; the Cd line 2573 was very weak

That is to say, no absorption bands were observed in the vapours of *o*- and *m*-di-iodobenzene, whereas a considerable number of bands were found in the vapours of the corresponding *o*- and *m*-dichloro- and dibromo-benzenes (*loc. cit.*).

Solutions in Alcohol: Iodobenzene.

TABLE VII.

The absorption spectra of solutions of iodobenzene have been investigated by Pauer (*loc. cit.*), who found no bands. The author has studied the absorption spectra of various strengths of alcoholic solutions of iodobenzene, and table VI describes the phenomena observed.

Strength of solution.	Thickness of solution in mm.	Limit of transmitted rays. λ.
M/10	2	2820
	10	2980
	20	3050
	30	3080
M/100	2	2400
	10	2730
	20	2800
	30	2850
M/1000	2	2330
	10	2380
	20	2410
	30	2500

That is to say, no bands were observed in alcoholic solutions of iodobenzene, whereas alcoholic solutions of each of the corresponding substances chloro- and bromo-benzenes exhibited seven bands, the two most refrangible bands being very weak (*loc. cit.*).

The following table (VIII) describes the absorption of various alcoholic solutions of *o*- and *m*-iodotoluene.

TABLE VIII.

o-Iodotoluene.			*m*-Iodotoluene.		
Strength of solution.	Thickness of solution in mm.	Limit of transmitted rays. λ.	Strength of solution.	Thickness of solution in mm.	Limit of transmitted rays. λ.
M/100	2	2410	*M*/100	2	2430
	10	2770		10	2800
	20	2820		20	2850
	30	2860		30	2880
M/1000	2	2350	*M*/1000	2	2360
	10	2400		10	2420
	20	2420		20	2440
	30	2500		30	2550

No bands of selective absorption were observed in any of the solutions, whereas alcoholic solutions of the corresponding chloro- and bromo-toluenes exhibited two wide diffuse bands and a very weak doubtful band on the more refrangible side (*loc. cit.*).

The following table (IX) describes the absorption of various alcoholic solutions of *o*- and *m*-di-iodobenzene.

TABLE IX

o-Di-iodobenzene.			*m*-Di-iodobenzene.		
Strength of solution.	Thickness of solution in mm.	Limit of transmitted rays. λ.	Strength of solution.	Thickness of solution in mm.	Limit of transmitted rays. λ.
M/100	2	2750	*M*/100	2	2730
	10	2980		10	2950
	20	3130		20	2990
	30	3240		30	3050
M/1000	2	2480	*M*/1000	2	2420
	10	2550		10	2470
	20	2690		20	2570
	30	2840		30	2750

No bands of selective absorption were observed, whereas alcoholic solutions of each of the corresponding dichloro- and dibromobenzenes showed four well-marked bands (*loc. cit.*); the fourth most refrangible band in each of the dibromobenzenes was very weak and difficult to distinguish.

Liquids in Thin Films.

Each liquid was pressed between two quartz plates, and held rigidly in front of the slit of the spectroscope. The radiant energy of the Cd spark was passed through the thin films for various periods of time varying from one minute to five minutes. As regards the two solids *o*- and *m*-di-iodobenzenes, the melting points of which are 27° and 40° respectively, a few crystals of each substance were placed on one of the quartz plates, which was warmed just to the melting point of the substance, and the other quartz plate was then pressed closely over the liquid. There was no crystallisation of either substance while the absorption was being photographed. The following table gives the limits of the transmitted rays through thin films of the various substances.

TABLE X.

	Time of exposure in in minutes.	Limit of transmitted rays. λ.
Iodobenzene	5	2600
o-Iodotoluene	5	2780
m-Iodotoluene	5	2820
o-Di-iodobenzene	5	2900
m-Di-iodobenzene	5	2850

In no case was any absorption band observed; whereas thin films of the corresponding chloro- and bromo-benzenes showed seven bands, the most refrangible in each case being very weak; the *o*- and

m-chloro- and bromo-toluenes showed two well-marked bands and a doubtful more refrangible third; the *o*- and *m*-dichloro- and -dibromo-benzenes showed three well-marked bands and a doubtful more refrangible fourth; and toluene exhibited three bands (*loc. cit.*).

Results and Conclusions.

The results of the preceding observations prove that in the ultra-violet regions neither the vapours, nor the alcoholic solutions, nor the thin films of the iodine derivatives of benzene or of toluene exhibit any bands of selective absorption, whereas the corresponding chlorine and bromine compounds have a well-marked series of bands under similar physical conditions.

The decrease in the number of vapour bands when the number and weight of the side-chains are increased is analogous to that observed by Hartley in the case of benzene and its homologues (*Phil. Trans.*, 1908, *A*, **208**, 475); for example, the maximum number of bands found in benzene by Hartley was 84, in toluene 22, in ethylbenzene 19, in *o*-xylene 23, in *m*-xylene 41, in *p*-xylene 30, in cymene 9, and in mesitylene 4. In the halogen derivatives the maximum number of bands found by the author (*loc. cit.*) in the vapour of chlorobenzene was 72, in bromobenzene 62, in *o*-dichlorobenzene 29, in *m*-dichlorobenzene 35, in *o*-dibromobenzene 30, in *m*-dibromobenzene 13, in *o*-chlorotoluene 23, in *m*-chlorotoluene 20, in *o*-bromotoluene 15, and in *m*-bromotoluene 19; so that the chief controlling factors are the type, weight, and orientation of the introduced radicles. Now when the heavy iodine atom takes the place of either chlorine or bromine, the bands completely disappear, and there is no selective absorption. Analogous phenomena are observed in the bands of the alcoholic solutions and of the thin films of these various substances. The few broad diffuse bands observed in the solutions and in the thin films of the chlorine and bromine derivatives completely disappear in the solutions and the thin films of the corresponding iodine compounds. At the same time, the differences in the positions where general absorption begins in equimolecular solutions of the ortho- and meta-compounds indicate that the orientation of the side-chain is a factor in determining the extent of the general absorption.

In previous communications (*loc. cit.*) the author has suggested an explanation to account for the facts observed in the chlorine and bromine compounds of benzene and toluene; and the phenomena observed in the corresponding iodine compounds appear to support that explanation. The heavy iodine atom is the controlling force, and it damps and dislocates the movements of the atoms of the benzene nucleus as well as the alkyl side-chains, so that the

rhythmical oscillations or vibrations are destroyed, and no selective absorption is possible. The dislocation of the oscillations occurs, not only when the vibrations are restricted, as in the alcoholic solutions and in the thin films, but also in the vapours where the vibrations are not subjected to any external forces except those of variations of temperature and pressure. Besides the mass of the atom, the action of the radiant energy may be a considerable factor in the final result; because each atom will absorb an amount of energy dependent on its intrinsic characters, and this will react on its own vibrations and on the vibrations of the other atoms. The final adjustment, therefore, will depend on the balance of a complex series of disturbances, and the forces which determine these include such factors as the number, the mass, the intrinsic characters, and the orientation of the atoms of both the nucleus and the side-chains; the physical conditions of the vibrating system as vapours or in solution or as liquids at various temperatures and pressures; and on the distribution and reaction of the vibrations consequent on the absorption of the radiant energy by the various oscillating atoms and atomic groups.

The author is engaged in a comparative study of naphthalene and anthracene and their derivatives, the results of which will be submitted later; and he desires to thank again the Government Grant Committee of the Royal Society, by whose assistance the larger portion of the cost of the apparatus was defrayed.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CCLVI.—*Influence of Double Linking on Optical Activity; Some* n-*Propyl and Allyl Derivatives of Menthol.*

By PERCY FARADAY FRANKLAND and HUGH HENRY O'SULLIVAN.

IN connexion with the problem of ascertaining the influence of double linking on optical activity it has been shown by one of us that both in the substitution of tartramide and of malamide by *n*-propyl and by allyl respectively the resulting *n*-propylamides have higher molecular rotations than the corresponding allylamides (P. Frankland and Twiss, Trans., 1906, **89**, 1854; and P. Frankland and Done, Trans., 1906, **89**, 1861), which is contrary to the generally

accepted rule that unsaturated groupings bring about a higher rotation than the corresponding saturated ones. This rule is based on results obtained in a number of investigations made during the past thirteen years by Tschugaeff (*Centralbl.*, 1898, **69**, I., 875; II., 404; 1902, **73**, II., 1238), Haller, Rupe (for many references to literature see Trans., 1903, **83**, 1351), Hilditch (Trans., 1908, **93**, 1909, **95**, 1910, **97**, 1911, **99**; *Zeitsch. physikal. Chem.*, 1911, **77**, 482), and others.

The present communication contains data obtained in the further investigation of this subject.

The compounds which we have prepared are three pairs of *n*-propyl and allyl derivatives of menthol; they were all liquids, and their rotations were determined at a number of different temperatures between 15° and 100°. Their rotations have also been determined in methyl alcohol solution.

In the following table we have recorded the values for $[M]_D^{20}$ in the liquid state, whilst we have included for comparison the corresponding values for some other *n*-propyl and allyl compounds.

	B. p.	$[M]_D^{20}$ in liquid state.
Menthoxyacetic allylamide,	185—187°/14 mm.	−192·5°
Menthoxyacetic propylamide	188—189°/16 mm.	193·7
Allyl menthoxyacetate	182°/40 mm.	234·4
Propyl menthoxyacetate	172°/26 mm.	234·1
Menthyl allylaminoacetate	155—157°/17 mm.	160·5
Menthyl propylaminoacetate	159—161°/17 mm.	158·3
Menthyl allyl ether *	—	$[M]_D^{19}$ −192·5
Menthyl propyl ether †	—	182·5

	M. p.	$[M]_D^{20}$ in pyridine solution.
Tartaric allylamide ‡	183°	+251°
Tartaric propylamide ‡	216	+289
Malic allylamide §	117·5	− 72·7
Malic propylamide §	126	90·5

* Haller and Marsch (*Compt. rend.*, 1904, **138**, 1665).

† Tschugaeff (*Centralbl.*, 1902, II, 1238).

‡ Frankland and Twiss (*loc. cit.*).

§ Frankland and Done (*loc. cit.*).

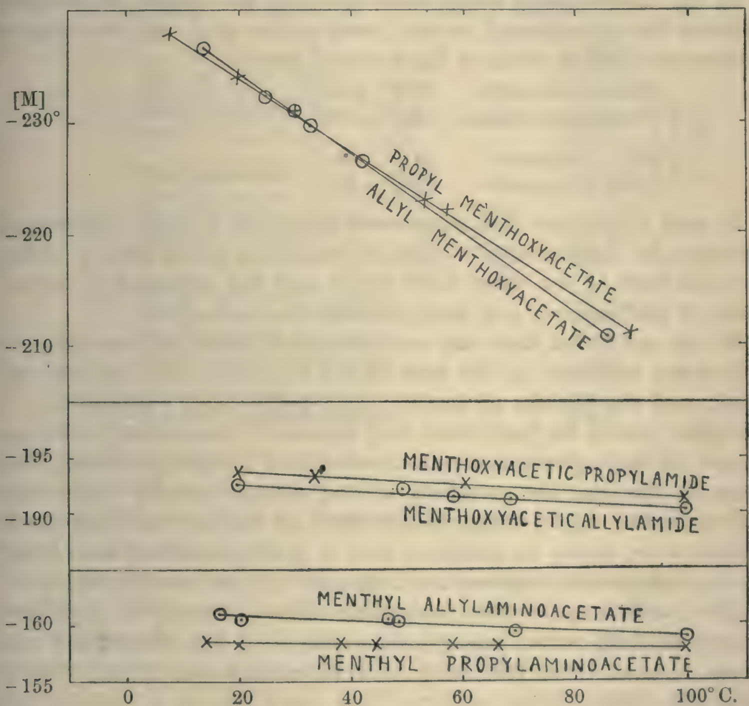
In the case of the amides of menthoxyacetic acid the allyl compound is seen to have the lower molecular rotation, but the difference is very small. This difference is practically the same over the range of temperature at which the observations were made. In this case the double linking diminishes the rotatory power, and agrees in this respect with the results obtained with the tartaric and malic amides.

The allyl and propyl esters of menthoxyacetic acid have practically identical molecular rotations at 20°, but whilst below 35° the

rotation of the allyl is very slightly in excess of that of the propyl compound, above that temperature the relation is reversed (see diagram).

In the case of the next pair, menthyl allylaminoacetate and propylaminoacetate, the allyl compound has slightly the higher molecular rotation throughout the whole range of temperature over which the observations were made.

Molecular rotation curves of the six compounds.



The results recorded in this paper lead to some general considerations:

(1) The extremely small differences between the molecular rotations of the pairs of allyl and propyl compounds described may be accounted for by the great distance of the unsaturated grouping in the allyl from the nearest asymmetric carbon atom in the menthyl radicle; thus, in menthoxyacetic allylamide, in allyl menthoxyacetate, and in menthylallylaminoacetate there are, in each case, *five atoms intervening between the unsaturated carbon atom of the allyl and the nearest asymmetric carbon atom of the menthyl.* That a constitutional change (such as passing from allyl to propyl)

made at such a great distance from the asymmetric carbon atom should have but little effect on the rotation is in accordance with the conclusions arrived at by P. Frankland and MacGregor (Trans., 1896, **69**, 121), and since confirmed by many other workers.

(2) Much greater differences in the molecular rotations of the following pairs of allyl and propyl compounds have been observed:

Liquid state.	Menthyl allyl ether	$[M]_D^{19}$	$-192 \cdot 5°$	Difference = 10°.
	Menthyl propyl ether	$[M]_D^{19}$	$-182 \cdot 5°$	

In the menthylallyl ether there are only two atoms intervening between the unsaturated carbon atom of the allyl and the nearest asymmetric carbon atom of the menthyl group.

Pyridine solution.	Tartaric allylamide	$[M]_D^{20}$	$+251°$	Difference = 38/2 = 19°.
	Tartaric propylamide	$[M]_D^{20}$	$+289°$	
	Malic allylamide	$[M]_D^{20}$	$-72 \cdot 7°$	Difference = 17·8°
	Malic propylamide	$[M]_D^{20}$	$-90 \cdot 5°$	

In each of the two allyl compounds there are 3 atoms intervening between the unsaturated carbon of one allyl group and 4 atoms between that of the other allyl group and the asymmetric carbon atom of the tartaric and malic radicles respectively.

We do not think that any comparisons between the quantitative differences obtained in the case of the menthyl ethers on the one hand, and the amides of tartaric and malic acids respectively on the other, would be justifiable, first, because of the entirely different nature of the asymmetric nuclei concerned in the two cases, and secondly, because the rotations of the menthyl ethers were determined in the liquid state, whilst those of the tartaric and malic amides were taken in solution, and a great variation was found in the differences between the rotations of the propyl- and allyl-amides according to the particular solvent employed (pyridine, methyl alcohol, water, and glacial acetic acid) (see Frankland and Twiss, Trans., 1906, **89**, 1853, and Frankland and Done, Trans., 1906, **89**, 1860).

(3) It will be seen that the menthoxyacetic grouping gives rise to a much higher molecular rotation than the menthyl aminoacetate grouping, and that the propyl and allyl esters of menthoxyacetic acid again have higher rotations than the corresponding propyl- and allyl-amides.

(4) In this connexion the following relations are worthy of note:

	$[M]_D^{20}$.
Menthyl allylaminoacetate	$-160 \cdot 5°$
Menthyl propylaminoacetate	158·3
Menthyl propionate *	160·2
"Normal constant of the menthyl homologous fatty esters" *	157·8
Menthyl phenylpropionate *	161·9

* Tschugaeff.

Thus, such profound differences in constitution as exist between the fatty acids on the one hand and the substituted amino-fatty acids on the other are attended with practically no alteration in the molecular rotation. These changes in constitution are ineffective, because occurring at a point remote from the asymmetric grouping.

(5) Again, the greater rotatory effect of the menthyl ether than of the menthyl ester grouping which we have found is in accordance with similar results obtained by Tschugaeff, thus:

	$[M]^{20}_{D}$.
Menthyl methyl ether	$-162·6°$
Menthyl ethyl ether	179·0
Menthyl propyl ether	182·5
Menthyl benzyl ether	232·7
Menthyl formate	146·3
Menthyl acetate	157·3
Menthyl propionate	160·2
Menthyl *n*-butyrate	156·9
Menthyl *n*-nonoate	157·3
Menthoxyacetic allylamide	192·5
Menthoxyacetic propylamide	193·7
Menthoxyacetic allyl ester	234·4
Menthoxyacetic propyl ester	234·1
Menthyl allylaminoacetate	160·5
Menthyl propylaminoacetate	158·3

From the above figures it will be seen incidentally that the acetic allyl ester and acetic propyl ester groupings have almost exactly the same rotatory effect as is exerted by the benzyl radicle in the series of menthyl ethers.

This greater rotatory effect of the menthyl ether than of the menthyl ester grouping is in reality a further illustration of what has been pointed out by Purdie and Irvine (Trans., 1901, **79**, 964) in respect of ethyl malate, ethyl monomethoxysuccinate, and ethyl acetylmalate on the one hand, and in respect of ethyl tartrate, ethyl dimethoxysuccinate, and ethyl diacetyltartrate on the other, and by P. Frankland and Gebhard (Trans., 1905, **87**, 864) in respect of the alkyl glycerates, alkyl dimethoxypropionates, and alkyl diacetylglycerates. In all of these cases the effect on molecular rotation of alkylating the OH-group attached to an asymmetric carbon atom is much greater than that produced by acetylating the same group.

Experimental.

Menthoxyacetic Acid, $C_{10}H_{19}·O·CH_2·CO_2H$.—Two hundred grams of menthol (Kahlbaum) were dissolved in about 500 c.c. of sodium-dried benzene in a 3-litre, round-bottom flask. Forty grams of

sodium cut up into thin plates were then added, and the flask was heated under a reflux condenser on a boiling-water bath for four hours. The excess of sodium was then removed (only 30 grams being required by 200 grams of menthol), and 50 grams of chloroacetic acid, dissolved in about 400 c.c. of dry benzene, were then added gradually, the flask being well shaken during the addition to keep the precipitated sodium chloroacetate in a finely divided state, and cooled when necessary to prevent violent boiling due to the reaction. The result of this is to produce a gelatinous precipitate of sodium chloroacetate, on which the sodium menthoxide is able to react to form the sodium salt of menthoxyacetic acid. It is apparent that two molecules of sodium menthoxide must be present for every molecule of chloroacetic acid, as the reaction takes place in two stages:

(1) $CH_2Cl{\cdot}CO_2H + NaO{\cdot}C_{10}H_{19} = CH_2Cl{\cdot}CO_2Na + C_{10}H_{20}O$.

(2) $CH_2Cl{\cdot}CO_2Na + NaO{\cdot}C_{10}H_{19} = C_{10}H_{19}{\cdot}O{\cdot}CH_2{\cdot}CO_2Na + NaCl$.

In the actual preparation the quantities taken were in the proportion of $2\frac{1}{5}$ molecules of sodium menthoxide to 1 molecule of chloroacetic acid. At first sight it would seem to be more economical were the sodium chloroacetate prepared in some other way instead of utilising sodium menthoxide as in the first equation, but this is practically the only serviceable way, and the excess of menthol is easy to recover.

The flask was then heated under a reflux condenser for twenty-five hours on a boiling-water bath. During this time the pasty sediment was periodically broken up by vigorous shaking, and dry benzene to the extent of $1\frac{1}{2}$ litres added at intervals to keep the mixture in a sufficiently liquid condition.

The sodium menthoxyacetate was then washed out with water, which also dissolves the sodium chloride, sodium hydroxide, and any free chloroacetic acid. The menthol remains in the benzene layer, as well as any tarry products if formed. The aqueous solution of sodium menthoxyacetate was acidified with sulphuric acid, and the free menthoxyacetic acid extracted with ether. This extract after being dried was concentrated to a syrup, which crystallised out in the refrigerator. The crystals were washed free from mother liquor with a little ether, and dried on porcelain.

This product was almost colourless, and melted only 3° below that of the purified acid. The total yield of this crude acid was 85 grams, which is 75 per cent. of the theoretical quantity obtainable from the chloroacetic acid used.

The acid is very soluble in all organic solvents; it was purified by repeated recrystallisation from ether. After six such crystallisa-

tions, the melting point was 53—54°, and the rotation in methyl alcohol at 20° was:

l.	p.	D^{20}_4.	c.	α_D.	$[\alpha]^{20}_D$.	$[M]^{20}_D$.
2-dcm.	5·253	0·8030	4·218	−7·84°	−92·93°	−198·8°

For the following preparations the acid was used after one crystallisation.

Menthoxyacetic Allylamide.—Ethyl menthoxyacetate was prepared by esterifying 60 grams of menthoxyacetic acid in an excess of absolute alcohol by saturation with dry hydrogen chloride. After heating for an hour, hydrogen chloride was again passed in, and the heating continued for another hour, after which the mixture was washed with a dilute solution of sodium carbonate, and the ester extracted with ether. After drying the extract, the ether was distilled over, and the ester distilled in a vacuum. The yield was 50 grams.

Fifteen grams of allylamine (Kahlbaum) were added, and the mixture heated under a reflux condenser on a water-bath for eight hours. The liquid product was purified by vacuum distillation until the observed rotation was constant. The yield was about 20 grams. After four distillations, the liquid boiled at 185—187°/14 mm., and gave $[\alpha]^{20}_D$ −76·11°.

The amide is a colourless, odourless, oily liquid, soluble in all organic solvents, but not in water or acids:

0·1466 gave 7·3 c.c. N_2 (moist) at 19° and 744·7 mm. N = 5·61.

$C_{15}H_{27}O_2N$ requires N = 5·53 per cent.

Densities:

t°.	20°.	30°.	50°	70°.	97°.
D^t_4	0·9667	0·9590	0·9442	0·9290	0·9082

Menthoxyacetic Allylamide.

Rotations in a 1-dcm. tube:

t°.	D^t_4 (from curve).	α^t_D.	$[\alpha]^t_D$.	$[M]^t_D$.
20	0·9667	−73·58°	−76·11°	−192·5°
49	0·9445	71·72	75·93	192·1
58	0·9376	70·97	75·70	191·5
68	0·9304	70·31	75·57	191·2
99	0·9070	68·20	75·19	190·2

Rotation in methyl alcohol solution. (Substance slightly impure through being kept a year.)

p.	c.	D^{20}_4.	α^{20}_D (l=2).	$[\alpha]^{20}_D$.	$[M]^{20}_D$.
2·3759	1·887	0·7944	−3·03°	−80·27°	−203·1°
3·9200	3·132	0·7990	5·02	80·13	202·7
7·1802	5·772	0·8039	9·14	79·18	200·3

Menthoxyacetic Propylamide.—This was prepared in an identical manner to the allylamide from 45 grams of the ester and 12 grams of propylamine (Kahlbaum). After five distillations the observed rotation not being constant, and there being only 12 grams of the purest fraction, a second preparation of the amide was commenced, and after five vacuum distillations was added to the first preparation. When the whole had been distilled three more times, the observed rotation became constant. The yield from the two preparations was 20 grams.

This pure substance boiled at 188—189°/16 mm., and gave $[\alpha]_D^{20}$ $-75·96°$. It is a colourless, odourless, oily liquid, similar in properties to the allylamide:

0·1410 gave 7·0 c.c. N_2 (moist) at 17·5° and 748·6 mm. N = 5·66.

$C_{15}H_{29}O_2N$ requires N = 5·49 per cent.

Densities:

$t°$.	20°.	30°.	50°.	70°.	97°.
D_4^t.	0·9545	0·9469	0·9320	0·9174	0·8958

Menthoxyacetic Propylamide.

Rotations in a 1-dcm. tube:

$t°$.	D_4^t. (from curve).	α_D.	$[\alpha]_D^t$.	$[M]_D^t$.
20·0	0·9545	−72·51°	−75·97°	−193·7°
33·5	0·9445	71·60	75·80	193·3
60·0	0·9240	69·83	75·57	192·7
99·0	0·8940	67·09	75·04	191·4

Rotation in methyl alcohol solution. (Substance slightly impure through being kept a year.)

p.	c.	D_4^{20}.	α_D^{20} (l=2).	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
2·3051	1·835	0·7960	−2·98°	−81·20°	−207·1°
4·5327	3·625	0·7997	5·88	81·11	206·8
6·0106	4·818	0·8016	7·79	80·84	206·1
7·3065	5·875	0·8041	9·44	80·34	204·9

Allyl Menthoxyacetate.—Sixty-five grams of menthoxyacetic acid (1 mol.) and 57 grams of allyl alcohol (3 mols.) were mixed in a flask and saturated with dry hydrogen chloride. After heating on a water-bath for a short time, more hydrogen chloride was passed in, and the mixture again heated for an hour. The mixture was then washed with a solution of sodium carbonate, and the ester and excess of allyl alcohol extracted with ether. This extract was dried, and the ether and alcohol distilled off. The ester was then distilled in a vacuum until the observed rotation was constant at 15° in a 0·5-dcm. tube. After seven distillations the ester boiled at 182°/40 mm., and gave $[\alpha]_D^{15}$ $-93·04°$. The yield was 20 grams.

This ester is a colourless, odourless, oily liquid, soluble in all organic solvents:

0·2758 gave 0·7130 CO_2 and 0·2559 H_2O. C=70·51; H=10·31.
$C_{15}H_{26}O_3$ requires C=70·87; H=10·23 per cent.

Densities:

$t°$.	15°.	20°.	30°.	40°.	60°.	80°.	99°.
D^t_4	0·9726	0·9682	0·9610	0·9528	0·9384	0·9222	0·9094

Allyl Menthoxyacetate.

Rotations in a 0·5-dcm. tube:

$t°$.	D^t_4 (from curve).	α_D.	$[\alpha]^t_D$.	$[M]^t_D$.
14	0·9720	−45·28°	−93·15°	−236·6°
25	0·9640	44·11	91·51	232·4
30	0·9605	43·66	90·91	230·9
33	0·9580	43·31	90·42	229·7
42	0·9515	42·45	89·23	226·6
85	0·9193	38·18	83·06	211·0

Rotation in methyl alcohol solution:

p.	D^t_4.	c.	l.	α_D.	$[\alpha]^{20}_D$.	$[M]^{20}_D$.
4·025	0·8003	3·221	2-dcm.	− 5·40°	−83·81°	−212·9°
8·912	0·8067	7·189	2-dcm.	12·06	83·87	213·0

Propyl Menthoxyacetate.—The propyl alcohol used had to be fractionated, as it boiled over a range of ten degrees, 93—103°. The fraction boiling at 96·5—97·5° was used for this preparation.

This ester was prepared in a similar manner to the above, excess of the alcohol to the extent of 3 molecules to 1 molecule of the menthoxyacetic acid being taken.

Seventy grams of the acid were esterified with 60 grams of propyl alcohol by means of dry hydrogen chloride, as for the above ester.

The crude ester, after seven distillations in a vacuum, had a constant rotatory power, $[\alpha]^{20}_D$ −91·46°, and boiled at 172°/26 mm. The yield was 19 grams.

The ester is a colourless, odourless, oily liquid, soluble in all organic solvents, but not in water:

0·2588 gave 0·6660 CO_2 and 0·2558 H_2O. C=70·18; H=10·98.
$C_{15}H_{28}O_3$ requires C=70·31; H=10·93 per cent.

Densities:

$t°$.	15°.	20°.	40°.	70°.	99°
D^t_4.	0·9577	0·9547	0·9381	0·9144	0·8901

Propyl Menthoxyacetate.

Rotations in a 0·5-dcm. tube:

$t°$.	D^t_4. (from curve.)	α_D.	$[\alpha]^t_D$.	$[M]^t_D$.
8·0	0·9638	−44·78°	−92·92°	−237·9°
20·0	0·9547	43·66	91·46	234·1
30·0	0·9461	42·71	90·30	231·2
53·0	0·9275	40·42	87·16	223·1
57·0	0·9240	40·15	86·91	222·5
89·5	0·8973	37·02	82·50	211·2

A 10·2 per cent. solution in methyl alcohol gave $[\alpha]^{20}_D$ −82·64°.

p.	D^t_4.	c.	l.	α_D.	$[\alpha]^{20}_D$.	$[M]^{20}_D$.
10·250	0·8057	8·258	2-dcm.	−13·65°	−82·64°	−211·5°

Menthyl Allylaminoacetate.—Forty grams of menthyl chloroacetate, prepared from menthol and chloroacetic acid by esterification with dry hydrogen chloride, were dissolved in 100 c.c. of sodium-dried ether, and 20 grams of allylamine were added. The mixture was heated under a reflux condenser for three hours on a water-bath. The interaction takes place readily, as after a few seconds crystals of allylamine hydrochloride were seen. It is necessary to take twice the quantity of amine required to replace the chlorine in the menthyl chloroacetate in order to combine with the hydrogen chloride split off.

The amine hydrochloride was quickly collected, and washed with a little dry ether. The weight—15 grams—showed that the interaction was complete. The ether and any excess of amine was distilled off, and the crude ester distilled in a vacuum until the observed rotation became constant. After four distillations the ester boiled at 155—157°/17 mm., and gave $[\alpha]^{20}_D$ −63·47°. The yield was 12 grams.

The ester is a colourless, odourless liquid, soluble in all organic solvents:

0·3552 gave 0·9206 CO_2 and 0·3374 H_2O. C=70·70; H=10·56.
0·2570 ,, 12·9 c.c. N_2 (moist) at 20° and 739·4 mm. N=5·58.
$C_{15}H_{27}O_2N$ requires C=71·15; H=10·67; N=5·53 per cent.

Densities:

$t°$.	12°.	20°.	40°.	69°.	100°.
D^t_4	0·9565	0·9488	0·9347	0·9133	0·8903

Menthyl Allylaminoacetate.

Rotations in a 0·5-dcm. tube:

t.	D^t_4. (from curve).	α_D.	$[\alpha]^t_D$.	$[M]^t_D$.
16·2	0·9518	−30·27°	−63·60°	−160·9°
20·5	0·9488	30·09	63·43	160·5
46·5	0·9295	29·49	63·45	160·5
48·5	0 9280	29·41	63 38	160·35
69·0	0·9133	28·76	62·98	159·3
99·8	0·8903	27·95	62·79	158·8

Rotations in methyl alcohol in a 2-dcm. tube at 20°:

D^t_4.	p.	c.	α_D.	$[\alpha]^{20}_D$.	$[M]^{20}_D$.
0·7945	1·5009	1·192	−1·70°	−71·28°	−180·33°
0·7979	3 0045	2·398	3·35	69·87	176·77
0·7993	4·1738	3·336	4·52	67·74	171·38

Menthyl Propylaminoacetate.—This was prepared in the same way as the above allylaminoacetic ester. Thirty-nine grams of menthyl chloroacetate were dissolved in 50 c.c. of dry ether, and heated with 20 grams of propylamine. After seven distillations in a vacuum the observed rotation was constant, the ester boiling at 159—161°/17 mm., and having $[\alpha]^{20}_D$ −62·03°. The yield was 6 grams.

This ester is colourless and odourless, and is soluble in all organic solvents:

0·3698 gave 0·9464 CO_2 and 0·3832 H_2O. C = 69·80; H = 11·51.
0·2590 „ 12·8 c.c. N_2 (moist) at 21° and 742·4 mm. N = 5·47.
$C_{15}H_{29}O_2N$ requires C = 70·59; H = 11·37; N = 5·49 per cent.

Densities:

$t°$.	12°.	20°.	40°.	69°.	100°.
D^t_4.	0·9406	0·9330	0·9185	0·8976	0·8753

Menthyl Propylaminoacetate.

Rotations in a 0·5-dcm. tube:

$t°$,	D^t_4 (from curve).	α_D.	$[\alpha]^t_D$.	$[M]^t_D$.
14·5	0·9368	−29·14°	−62·21°	−158·6°
20·0	0·9330	28·96	62·08	158·3
38·0	0·9195	28·55	62·10	158·4
44·5	0·9152	28·40	62·06	158·3
58·0	0·9052	28·08	62·04	158·2
66·0	0·8995	27·86	61·95	158·0
99·0	0·8756	27·10	61·90	157·8

Rotations in methyl alcohol in a 2-dcm. tube at 20°:

D_4^t	p.	c.	a.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
0·7969	2·9900	2·383	−3·32°	−69·67°	−177·6°
0·7989	4·5608	3·644	5·04	69·16	176·3
0·8057	8·9275	7·193	9·87	68·61	174·9

Chemical Laboratories, University,
Edgbaston, Birmingham.

CCLVII.—*The Constitution of Ergothioneine: a Betaine Related to Histidine.*

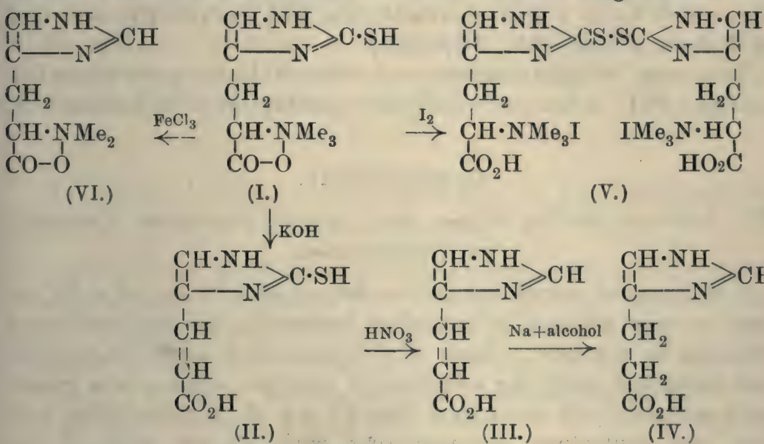
By George Barger and Arthur James Ewins.

Two years ago Tanret (*J. Pharm. Chim.*, 1909, [vi], **30**, 145) isolated from ergot a new crystalline base containing sulphur, and having the formula $C_9H_{15}O_2N_3S$. The description of the base given by Tanret suggested to us a possible relationship to the amino-acid histidine; thus ergothioneine, as the new base was called by Tanret, is precipitated by mercuric chloride, and forms a compound with silver. These properties, together with the large nitrogen content, were strongly suggestive of the presence of a glyoxaline ring. Since one of us in conjunction with H. H. Dale (Trans., 1910, **97**, 2592) had already isolated another histidine derivative from ergot, namely, 4(or 5)-β-aminoethylglyoxaline, a substance of great physiological activity and interest, we prepared a small quantity of ergothioneine according to Tanret's method, and found that, like histidine and many other glyoxaline derivatives, it gives an intense red coloration with sodium *p*-diazobenzenesulphonate, thus still further supporting our surmise with regard to the constitution of this base.

Ergothioneine contains (in addition to the sulphur atom) three carbon atoms and six hydrogen atoms more than histidine. These might well result from the substitution of three hydrogen atoms of histidine by methyl groups in such a manner that ergothioneine would be a new member of the class of methylated amino-acids or betaines, of which a number of examples are now known to occur in plants. This hypothesis proved to be correct; the substance is indeed a betaine, and almost certainly β-2-thiolglyoxaline-4(or 5)-propiobetaine (I). Like other betaines it has no marked physiological action.

On boiling with a concentrated (50 per cent.) aqueous solution of potassium hydroxide, the base is decomposed quantitatively into

trimethylamine and a yellow acid of the composition $C_6H_6O_2N_2S$, which represents the whole of the remaining atoms in the molecule, and the constitution of which is represented by (II). On boiling with dilute nitric acid, the sulphur atom of this acid is completely removed, and a new acid, β-glyoxaline-4(or 5)-acrylic acid (III), is formed. This acid on reduction yields β-glyoxaline-4(or 5)-propionic acid (IV), and we were able to identify both the saturated and the unsaturated acid by comparison with synthetic specimens. The various reactions will be best seen from the following scheme:



The only doubtful point remaining was with regard to the position of the sulphur atom. There are two probable positions, namely, attachment to the β-carbon atom of the side-chain or to the carbon atom in the 2-position in the glyoxaline ring, and choice between these two, although decisive, is based on analogy rather than on direct evidence; indeed, synthesis seems to be the only means of supplying complete proof.

The sulphur in ergothioneine reacts in every way like that of the thiolglyoxalines, and quite different from that in cystein, with which it might be expected to show analogies if attached to the β-carbon atom of the side-chain; thus the sulphur in cystein, as is well known, is readily eliminated by boiling with sodium hydroxide, whereas, as was stated above, the sulphur of ergothioneine is not removed by boiling with the strongest solutions of potassium hydroxide. On the other hand, the sulphur atom, like that of the thiolglyoxalines, is readily and quantitatively oxidised by ferric chloride (as recently employed by Pyman) or by bromine water to sulphuric acid, whereas in the case of cystein a sulphonic acid results, in which the sulphur still remains attached to the carbon atom. The only oxidising agent which acts similarly on cystein and ergo-

thioneine is iodine, which oxidises both to a compound, in which two sulphur atoms are directly linked. That obtained from ergothioneine has the constitution (V).* A further argument for considering ergothioneine to be a thiolglyoxaline derivative is the fact that, like other betaines, it is a feeble mono-acid base, whereas we should expect it to be di-acid if it, like histidine, contained the simple glyoxaline ring. The basic properties of the ring are destroyed by the presence of the sulphur atom as in other thiolglyoxalines (compare, for instance, 2-thiol-4(or 5)-aminomethylglyoxaline, which forms a mono-hydrochloride, and was recently described by Pyman, Trans., 1911, **99**, 672).†

Treatment of ergothioneine with ferric chloride gave trimethylhistidine (VI), a betaine which may possibly occur in nature.

Experimental.

The Action of Boiling 50 *per cent. Aqueous Potassium Hydroxide on Ergothioneine.*

0·88 Gram of ergothioneine was boiled with 20 c.c. of a 50 per cent. aqueous solution of potassium hydroxide, the distillate being collected in a known volume of *N*-hydrochloric acid. Distillation was continued until the evolution of alkaline vapours was practically complete. It was found that 3·1 c.c. of *N*-hydrochloric acid had been neutralised, corresponding with 80 per cent. of the theoretical for the evolution of one nitrogen atom. The main bulk of the distillate was evaporated to dryness, and the residue dissolved in a little alcohol and treated with an alcoholic solution of platinic chloride, when trimethylamine platinichloride (m. p. 241°) separated. (Found, Pt=36·9. Calc., Pt=36·9 per cent.)

One nitrogen atom was thus shown to be evolved as trimethylamine. The strongly alkaline residue in the flask was rendered acid to Congo-red, when there was at once precipitated as a yellow, amorphous solid, β-2-*thiolglyoxaline*-4-*acrylic acid.*

This acid was found to be characterised by its general insolubility.

* This iodide will be described later. It was already obtained by Tanret, who did not, however, appreciate its true significance. It forms black, steel grey or blue mixed crystals with iodine, a peculiar and extremely rare property which has so far only been observed in the case of cholalic acid, narceine, and saponarin, and is closely analogous to the adsorption of iodine by starch. For this reason Tanret, who analysed the compound, did not obtain results in agreement with any simple formula.

† Dr. Pyman has since informed us of his recent observation that thiolglyoxalines are sharply differentiated from glyoxalines by the fact that they at once decolorise a dilute cold solution of potassium permanganate; we find that ergothioneine also does this, but histidine does not, nor does cystine.

It is only moderately soluble in pyridine, and almost insoluble in all other ordinary organic solvents. The acid was crystallised for analysis by making a very dilute solution (0·1 per cent.) of the sodium salt, and acidifying. After three or four hours the acid began to separate, and precipitation was complete in about thirty-six hours. The acid obtained in this way separated in clusters of small prisms, which did not melt below 275°:

0·1179 gave 0·1805 CO_2 and 0·0420 H_2O. C=41·8; H=3·9.
$C_6H_5O_2N_2S$ requires C=42·3; H=3·5 per cent.

By oxidation by means of dilute nitric acid as described below, 90 per cent. of the theoretical amount of sulphur was obtained from the filtrate as barium sulphate.

The Action of Boiling Dilute Nitric Acid on β-2-Thiolglyoxaline-4-acrylic Acid.

0·4 Gram of amorphous β-2-thiolglyoxaline-4-acrylic acid was added in small portions to 20 c.c. of 10 per cent. aqueous nitric acid. The mixture was kept gently boiling on a sand-bath for some minutes after solution was complete, and then allowed to cool. The crystalline *nitrate* of *β-glyoxaline*-4(or 5)-*acrylic acid* separated out, which after washing and drying melted at 198° with explosive decomposition. The yield was 0·28 gram:

0·1114 gave 0·1470 CO_2 and 0·0404 H_2O. C=36·0; H=4·0.
$C_6H_6O_2N_2,HNO_3$ requires C=35·8; H=3·5 per cent.

β-Glyoxaline-4(or 5)-*acrylic acid* was most readily obtained from the nitrate by the addition of one equivalent of sodium carbonate (solid) to a concentrated aqueous solution of the salt, when the acid separates at once as a crystalline solid, which after recrystallisation from dilute acetone was quite pure, and melted at 235—236°:

0·1776 gave 0·3474 CO_2 and 0·0712 H_2O. C=53·3; H=4·4.
$C_6H_6N_2O_2$ requires C=52·2; H=4·3 per cent.

β-Glyoxaline-4(or 5)-acrylic acid is moderately soluble in cold, but very readily so in hot, water. Its solutions give an intense red colour with sodium *p*-diazobenzenesulphonate.

The *phosphotungstate* is readily soluble in hot water or cold acetone, and crystallises in small, rectangular plates from dilute acetone.

The *picrate* forms golden-yellow prisms, melting at 213—214°, and sparingly soluble in cold water. The melting point of this picrate

remained unchanged when mixed with a synthetic specimen. The latter we obtained in small quantity by the action of trimethylamine on α-chloro-β-glyoxaline-4(or 5)-propionic acid.

*The Reduction of β-Glyoxaline-*4(or 5)*-acrylic Acid to β-Glyoxaline-*4(or 5)*-propionic Acid.*

β-Glyoxaline-4(or 5)-acrylic acid was dissolved in a little absolute alcohol, and the hot solution treated with five to six atomic proportions of sodium. The solution was then acidified with hydrochloric acid, and the precipitated salt collected. The filtrate and washings were evaporated to dryness, the residue dissolved in 5 per cent. aqueous sulphuric acid, and precipitated with phosphotungstic acid. The precipitate was treated with acetone, filtered from undissolved material, and the soluble phosphotungstate decomposed in the usual manner. On concentrating the final filtrate a crystalline acid separated, which after recrystallisation melted at 202°. When mixed with a specimen of synthetic β-glyoxaline-4(or 5)-propionic acid (m. p. 202°), the melting point remained unaltered. The acid obtained on reduction was therefore proved to be β-glyoxaline-4(or 5)-propionic acid.

*The Action of Ferric Chloride on Ergothioneine. Formation of β-Glyoxaline-*4(or 5)*-propiobetaine (Histidine-betaine).*

One gram of ergothioneine was boiled for one hour with an aqueous solution containing nine molecular proportions of ferric chloride. The iron was removed from solution by sodium carbonate, the filtrate acidified with sulphuric acid (so as to give a 5 per cent. solution of the latter), and precipitated by phosphotungstic acid. The precipitate, which was completely soluble in acetone, was decomposed in the usual way, and the barium and sulphuric acid removed. The filtrate was concentrated, and treated with a hot aqueous solution of picric acid. On cooling, a crystalline picrate separated, which after recrystallisation from water was obtained in deep yellow prisms melting at 123°:

0·1340 gave 0·1908 CO_2 and 0·0396 H_2O. C=38·4; H=3·3.

$C_9H_{15}O_2N_3(C_6H_3O_7N_3)_2$ requires C=38·5; H=3·3 per cent.

The *dipicrate* is very sparingly soluble in cold, fairly readily so in hot, water.

The *picrolonate* prepared in the usual way forms long, thin, orange-yellow needles, melting at 229—230°.

The *aurichloride* separated from dilute aqueous hydrochloric acid as large, broad, deep orange-yellow prisms, melting at 171°.

In conclusion, we wish to express our indebtedness to Dr. F. L. Pyman for synthetic specimens of α-chloro-β-glyoxaline-4(or 5)-propionic and β-glyoxaline-4(or 5)-propionic acids for purposes of comparison, and to the Wellcome Chemical Works, Dartford, for a supply of ergothioneine.

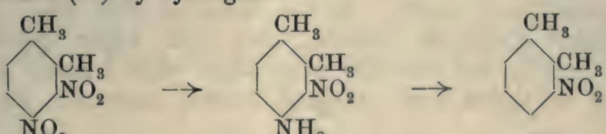
THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
BROCKWELL HALL, HERNE HILL, LONDON, S.E.

CCLVIII.—*Derivatives of* o-*Xylene. Part I.* 3-*Nitro*-o-*xylene and* 3 : 6-*Dinitro*-o-*xylene.*

By ARTHUR WILLIAM CROSSLEY and GERTRUDE HOLLAND WREN.

IN 1909 an account of the preparation and properties of 3-nitro-*o*-xylene was published (Trans., **95**, 208). The method adopted for its isolation (*ibid.*, p. 216) consisted in treating *o*-xylene with a mixture of nitric and sulphuric acids and separating the two mono-nitro-*o*-xylenes from the dinitro-*o*-xylenes by distillation. The mixture of 3- and 4-nitro-*o*-xylenes was then distilled fractionally, and each fraction cooled, when 4-nitro-*o*-xylene separated as a yellow solid, melting at 30°. After repeating this process several times, the residual liquid product was refractioned, when finally an oil, boiling at 131°/20 mm., was obtained, which was proved to be 3-nitro-*o*-xylene by the fact that it gave on oxidation an almost quantitative yield of 3-nitrophthalic acid. Nevertheless, the method of preparation is not without objection, for despite the numerous fractional distillations carried out, it is possible that the resulting 3-nitro-*o*-xylene might contain a small quantity of 4-nitro-*o*-xylene dissolved in it, and it seemed of interest to prepare 3-nitro-*o*-xylene by some other method, in which the isomeric 4-nitro-*o*-xylene would not be produced, and to compare the physical constants of the two specimens of 3-nitro-*o*-xylene.

The method adopted was to replace the amino-group in 3-nitro-*o*-4-xylidine (II) by hydrogen:



(I.) (II.) (III.)

3-Nitro-*o*-4-xylidine (II) has been described by Noelting, Braun, and Thesmar (*Ber.*, 1901, **34**, 2249), and that these authors orien-

tated this compound correctly receives confirmation from the experiments now described. They prepared it by the action of a mixture of nitric and sulphuric acids on *o*-4-xylidine. The same substance may be more easily obtained by reducing 3:4-dinitro-*o*-xylene (I) with alcoholic stannous chloride, for which purpose 10 grams of 3:4-dinitro-*o*-xylene (Trans., 1909, **95**, 210) were suspended in 75 c.c. of absolute alcohol, and a solution of 40 grams of stannous chloride in 200 c.c. of absolute alcohol, saturated with dry hydrogen chloride, gradually added, the temperature being maintained between 10° and 12°. After remaining twenty-four hours the major portion of the alcohol was evaporated, and the residue poured into water, when on some occasions it was found necessary to filter from a small amount of unchanged dinitroxylene. Solid potassium hydroxide was then added until the precipitate originally formed, redissolved, when the nitroamine separated. This was extracted with ether, etc., when the residue, weighing 7·5 grams, solidified. It was purified by crystallisation from dilute alcohol, yielding 4·6 grams of 3-nitro-*o*-4-xylidine (compare Noelting, Braun, and Thesmar, *loc. cit.*) as scarlet-coloured needles, melting at 65—66°. On evaporating the alcoholic mother liquor and submitting the residue to steam distillation, a further 1·3 grams of the pure nitroamine were isolated, thus making the total yield 72 per cent. of that theoretically capable of being formed from the dinitroxylene employed. Although indications of the presence of the isomeric 4-nitro-*o*-3-xylidine were obtained, this substance has not, so far, been isolated in a pure condition.

3-*Nitro*-o-*xylene from* 3-*Nitro*-o-4-*xylidine*.

Two quantities of 5 grams of pure 3-nitro-*o*-4-xylidine were powdered and separately dissolved in a mixture of 30 c.c. of concentrated sulphuric acid and 5 c.c. of water, cooled in ice, and a solution of 2·1 grams of sodium nitrite in 10 c.c. of water gradually added, the temperature not being allowed to rise above 5°. The whole was then poured into 200 c.c. of boiling ethyl alcohol, heated for half an hour, the major portion of the alcohol evaporated, and the residue distilled in a current of steam, when an oil passed over readily. It was extracted with ether, washed with sodium hydroxide solution, then with water, dried over calcium chloride, and the ether evaporated, when 7 grams (theory, 9 grams) of liquid were obtained, boiling constantly at 136°/29 mm.:

0·2017 gave 15·8 c.c. N_2 (moist) at 17° and 762 mm. N = 9·11.

$C_8H_9O_2N$ requires N = 9·27 per cent.

3-*Nitro-o-xylene* is a clear, pale yellow, refractive liquid boiling at 240°/760 mm., solidifying on cooling, and melting sharply at 15°. When dissolved in alcohol and the solution cooled in ice, it crystallises readily in radiating clusters of almost colourless, transparent needles.

A comparison of the properties of pure 3-nitro-*o*-xylene with those of the substance previously described is given in the following table, from which it is evident that the latter was not quite pure, although, considering its method of preparation, its comparative purity is rather remarkable.

	Source.	B. p.	B. p.	M. p.
3-Nitro-*o*-xylene	Xylene + HNO_3 + H_2SO_4	245—246°/ 760 mm.	131°/20 mm.	7—9°
3-Nitro-*o*-xylene	3 : 4-Dinitro-*o*-xylene	240°/760 mm.	136°/29 mm.	15°

In order to obtain some idea of the amount of 4-nitro-*o*-xylene contained in the 3-nitro-*o*-xylene prepared by the action of a mixture of nitric and sulphuric acids on *o*-xylene, the melting points of mixtures of 3-nitro-*o*-xylene with definite amounts of 4-nitro-*o*-xylene were determined.

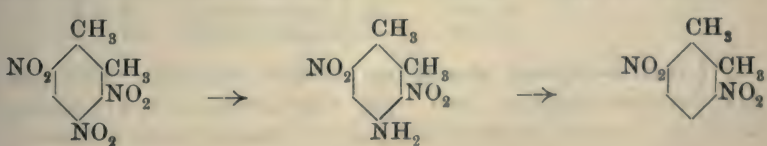
	Melting point.
3-Nitro-*o*-xylene, *pure*	15°
,, +1 per cent. of 4-nitro-*o*-xylene	12—14°
,, +2 ,, ,,	11·5—13·5°
,, +5 ,, ,,	9—11°
,, +10 ,, ,,	5—8°

From these figures it would appear that the 3-nitro-*o*-xylene prepared from *o*-xylene by the action of nitric and sulphuric acids contains about 7 per cent. of 4-nitro-*o*-xylene.

3 : 6-*Dinitro-o-xylene.*

The preparation of 3 : 6-dinitro-*o*-xylene by the nitration of 3-nitro-*o*-xylene has been described (Trans., 1909, **95**, 210), but as the substance was produced in such minute quantities the properties ascribed to it were given with some reserve. Experiments with much larger quantities of material have now been carried out, and the substance has been obtained pure.

Attempts to prepare 3 : 6-dinitro-*o*-xylene by the elimination of the nitro-group in position 4 from 3 : 4 : 6-trinitro-*o*-xylene did not give the desired result (compare this vol., p. 2345), but it has now



been isolated in a pure condition by further nitrating 3-nitro-*o*-xylene, and also from the residues obtained in the preparation of 3:4-dinitro-*o*-xylene (*ibid.*, p. 216), which residues contain about 0·3 to 0·5 per cent. of 3:6-dinitro-*o*-xylene.

Nitration of 3-Nitro-o-xylene.—Sixty grams of 3-nitro-*o*-xylene were nitrated and worked up as already described (Trans., 1909, **95**, 214) to give the substance of a waxy nature, melting at 56—60° (1·1 grams), previously stated to be 3:6-dinitro-*o*-xylene. On further crystallisation from alcohol it gave a small amount of a substance melting sharply at 89—90°, which, as shown later, is the true melting point of 3:6-dinitro-*o*-xylene.

Nitration of o-Xylene.—It has been shown (*ibid.*, p. 216) that when *o*-xylene is nitrated with fuming nitric acid, there are produced 3:4-dinitro-*o*-xylene, 4:6-dinitro-*o*-xylene, a mixture of 4:5-dinitro-*o*-xylene and 3:4-dinitro-*o*-xylene of constant melting point, and a waxy solid of low melting point. It was thought from its nature that the latter substance would contain 3:6-dinitro-*o*-xylene, and such has been proved to be the case. To isolate it 1250 grams of *o*-xylene were nitrated in quantities of 25 grams at one time, and the resulting solid worked up (*ibid.*, p. 212) for the separation of the dinitro-*o*-xylenes by alternate treatment with sulphuric acid and then alcohol, involving between five hundred and six hundred crystallisations from either sulphuric acid or alcohol. In this manner nearly 300 grams of the waxy solid of low melting point were obtained, which in quantities of 20 grams at one time were again submitted to fractional crystallisation from sulphuric acid and then alcohol (two hundred crystallisations), when 65 grams were obtained, melting at 50—60°. This latter substance was finally fractionated (one hundred crystallisations) from alcohol, when 3 grams of solid were obtained, melting sharply at 89—90°:

0·1355 gave 16·8 c.c. N_2 (moist) at 758 mm. and 20°. N=14·14.

$C_8H_8O_4N_2$ requires N=14·29 per cent.

3:6-*Dinitro-o-xylene* is very soluble in the cold in the ordinary organic solvents, except alcohol, from which it crystallises in sheaves of small needles melting at 89—90°. It is not identical with any of the other three dinitro-*o*-xylenes, as proved by the following mixed melting-point determinations:

	M. p.		M. p.	Mixed m. p.
3 : 6-Dinitro-*o*-xylene	89—90°	3 : 4-Dinitro-*o*-xylene	82°	59—62°
,,	89—90	3 : 5-Dinitro-*o*-xylene	75	48—52
,,	89—90	4 : 5-Dinitro-*o*-xylene	115	60—66

3:6-Dinitro-*o*-xylene should on further nitration yield only 3:4:6-trinitro-o-xylene, and not the isomeric 3:4:5-trinitro-*o*-xylene. In order to prove this point, 1 gram of pure 3:6-dinitro-

o-xylene was further nitrated by treatment with fuming nitric acid, when 1·2 grams (theory, 1·22 grams) of trinitro-*o*-xylene were

obtained, which after crystallisation from alcohol melted at 72°, nor was any trace of the isomeric trinitro-*o*-xylene, melting at 115°, isolated, although, as already shown, the separation of the two isomeric trinitro-*o*-xylenes is a very simple process.

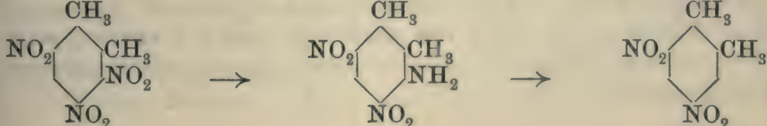
RESEARCH LABORATORIES, PHARMACEUTICAL SOCIETY,
17, BLOOMSBURY SQUARE, W.C.

CCLIX.—*Derivatives of* o-*Xylene. Part II. Dinitro*-o-*xylidines.*

By ARTHUR WILLIAM CROSSLEY and GEORGE FRANCIS MORRELL.

THE experiments described in this communication originated with the desire to find a method for preparing 3:6-dinitro-*o*-xylene which would be less tedious and give larger yields than that described on p. 2343 of this volume.

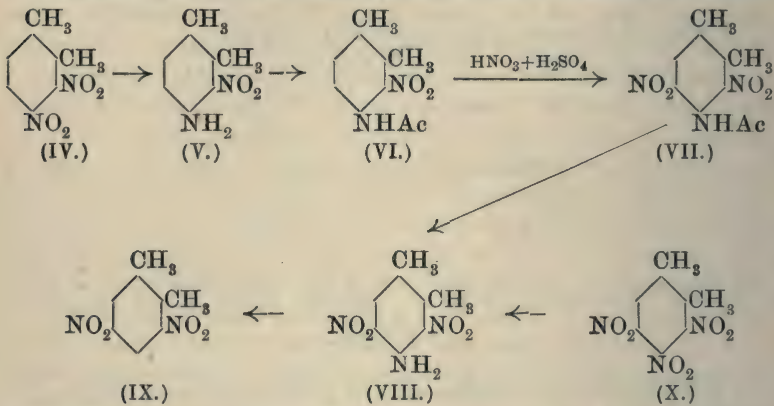
In the first place, the action of reducing agents on 3:4:6-trinitro-*o*-xylene (I) was tried in the hope that it might be found possible to convert the nitro-group in position 4 into an amino-group, which could then be replaced by a hydrogen atom. Reduction with ammonium sulphide gave rise entirely to sulphur compounds, which were not further examined, and stannous chloride gave equally unsatisfactory results. Alcoholic ammonia, however, reduced 3:4:6-trinitro-*o*-xylene readily, but the nitro-group in position 3



(I.) (II.) (III.)

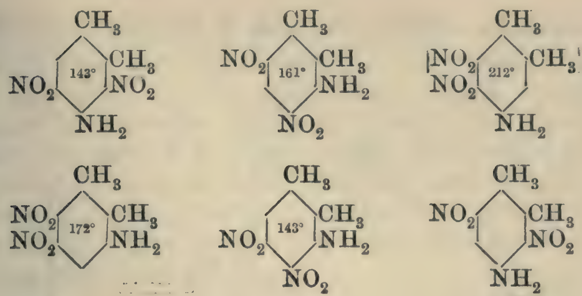
was the one to be attacked, and there resulted 4:6-dinitro-*o*-3-xylidine (II), which is proved by the fact that when the dinitroamine is diazotised and the diazo-group replaced by a hydrogen atom, 4:6-(3:5)-dinitro-*o*-xylene (III) is produced. The nitro-*o*-xylenes mentioned in this communication were described in the Transactions, 1909, **95**, 202.

The next attempt consisted in nitrating 3-nitroaceto-*o*-4-xylidide (VI), which was prepared by acetylating 3-nitro-*o*-4-xylidine (V), obtained by the reduction of 3:4-dinitro-*o*-xylene (IV), with stannous chloride, but the nitro-group, instead of entering position 6, as was thought possible, takes up position 5, giving 3:5-dinitroaceto-*o*-4-xylidide (VII). The constitution of this substance was estab-



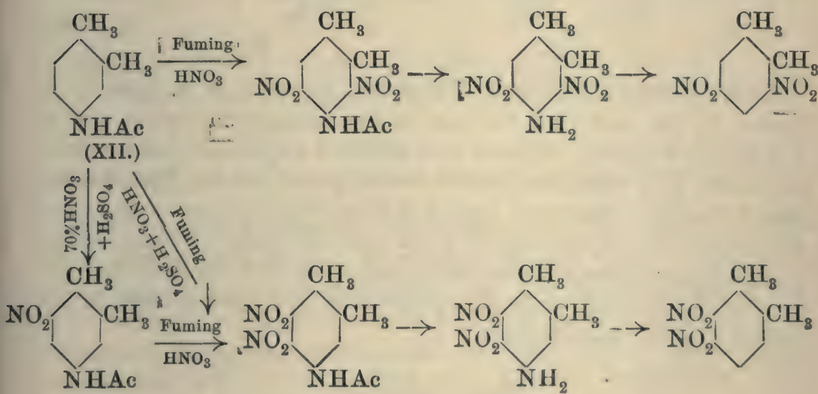
lished by removal of the acetylamino-group, when 3:5-dinitro-*o*-xylene (IX) is obtained. 3:5-Dinitro-*o*-4-xylidine is also produced by the reduction of 3:4:5-trinitro-*o*-xylene (X) with alcoholic ammonia.

Having proceeded so far, it seemed of interest to attempt the preparation of all the six possible dinitro-*o*-xylidines which on theoretical grounds should exist. Five of them are now described, the missing 3:6-dinitro-*o*-4-xylidine (XI) being the one which it was desired to prepare for the initial object of this research. In the reactions which have been tried, wherever it was possible for two different dinitroamines to result, evidence was forthcoming to show that both isomerides were formed, although one of the two was always obtained in largely predominating amount. It is therefore quite possible that 3:6-dinitro-*o*-4-xylidine is produced in some of these reactions, but under the conditions tried the amount must have been extremely small, and its isolation for all practical purposes an impossibility.



(XI.)

The next series of reactions consisted in nitrating aceto-*o*-4-xylidide (XII) under varying conditions, and the results are readily followed on consulting the accompanying diagram:

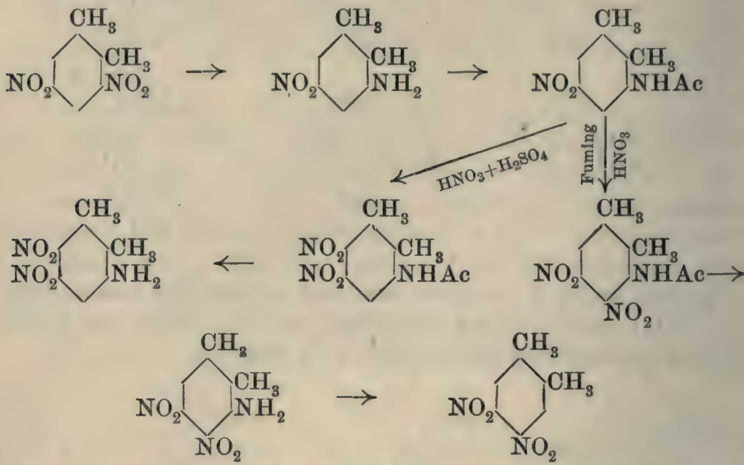


The product with fuming nitric acid alone, after elimination of the acetyl group, is identical with the substance obtained by the action of alcoholic ammonia on 3:4:5-trinitro-*o*-xylene, and is therefore 3:5-dinitro-*o*-4-xylidine.

A mixture of nitric and sulphuric acids gives a new dinitroamine, in which the position of the nitro-groups was ascertained by elimination of the amino-group, when 5:6-(3:4)-dinitro-*o*-xylene resulted. The dinitroamine is therefore 5:6-dinitro-*o*-4-xylidine, which can also be prepared from aceto-*o*-4-xylidide by first treating it with a mixture of 70 per cent. nitric acid and sulphuric acid, and nitrating the resulting 6-nitroaceto-*o*-4-xylidide with fuming nitric acid (compare Noelting, Braun, and Thesmar, *Ber.*, 1901, **34**, 2251).

Two other dinitro-*o*-xylidines were obtained by nitrating 5-nitro-

aceto-*o*-3-xylidide, involving the series of reactions indicated by the following formulæ:



With fuming nitric acid 4:5-dinitro-*o*-3-xylidine is formed, as proved by the fact that removal of the amino-group gives rise to 4:5-dinitro-*o*-xylene, whereas 5:6-dinitro-*o*-3-xylidine results from the action of a mixture of nitric and sulphuric acids. This dinitro-amine was not converted into a dinitro-*o*-xylene, for as only two dinitro-*o*-xylidines can result from the nitration of 5-nitroaceto-3-*o*-xylidide and the constitution of one of the two has been decided, no doubt can exist as to the position of the nitro-groups in the second product of nitration.

Experimental.

Reduction of 3:4:6-*Trinitro-o-xylene.*

3:4:6-Trinitro-*o*-xylene in quantities of 10 grams at one time was suspended in 100 grams of absolute alcohol, and dry ammonia passed in until the solution was saturated. The liquid first turned blue, then deep purple, changing to deep red as the trinitro-*o*-xylene passed into solution. The whole was allowed to remain for twenty-four hours, when a bronze-green, crystalline solid (7 grams) had separated. This was collected, and extracted with boiling alcohol, when 5·2 grams of fine, yellow needles were obtained. The insoluble residue was not further examined:

0·1909 gave 0·3208 CO_2 and 0·0720 H_2O. C=45·73; H=4·19.

0·1188 „ 20·3 c.c. N_2 (moist) at 20° and 757 mm. N=19·60.

$C_8H_9O_4N_3$ requires C=45·50; H=4·26; N=19·90 per cent.

4:6-*Dinitro*-o-3-*xylidine* is readily soluble in cold acetone or on warming in ethyl acetate, chloroform, or benzene, and crystallises from alcohol in fine, golden-yellow needles, melting at 161°.

The *diacetyl* derivative, prepared by heating the amine with a mixture of equal parts of acetyl chloride and acetic anhydride on the water-bath for three hours, is readily soluble in the cold in chloroform, readily on warming in benzene, ethyl acetate, or acetone, and crystallises from alcohol in large, transparent, fern-like aggregates, melting at 139°:

0·1741 gave 21·2 c.c. N_2 (moist) at 15° and 758 mm. N = 14·22.
$C_{12}H_{13}O_6N_3$ requires N = 14·24 per cent.

To determine the number of acetyl groups, the substance was hydrolysed with alcoholic potassium hydroxide, the alcohol evaporated, the residue acidified with sulphuric acid, distilled in a current of steam, and the acetic acid titrated with *N*/10-sodium hydroxide solution:

0·8413 required 0·232 gram NaOH. $CH_3·CO$ = 29·6.
$C_8H_7O_4N_3(CH_3·CO)_2$ requires $CH_3·CO$ = 29·1 per cent.

Conversion of 4:6-*Dinitro*-o-3-*xylidine into* 4:6-*Dinitro*-o-*xylene*.

Four grams of 4:6-dinitro-*o*-3-xylidine were dissolved in a mixture of 24 c.c. of concentrated sulphuric acid and 4 c.c. of water, the whole cooled in a freezing mixture, and the calculated quantity of a 20 per cent. solution of sodium nitrite gradually added (compare Blanksma, *Rec. trav. chim.*, 1909, **28**, 93). The whole was then poured into 100 c.c. of boiling ethyl alcohol, heated for thirty minutes, poured into water, and the precipitated solid crystallised from alcohol, when it melted at 75°; nor was this melting point lowered on mixing with pure 4:6-dinitro-*o*-xylene:

0·1011 gave 12·6 c.c. N_2 (moist) at 18° and 761 mm. N = 14·40.
$C_8H_8O_4N_2$ requires N = 14·29 per cent.

Reduction of 3:4:5-*Trinitro*-o-*xylene*.

Ten grams of 3:4:5-trinitro-*o*-xylene were reduced with alcoholic ammonia as described in the case of the isomeric trinitroxylene (see p. 2348), when 8·8 grams of crude material were obtained. No part of the reduction product was insoluble in alcohol:

0·1100 gave 18·8 c.c. N_2 (moist) at 20° and 768 mm. N = 19·76.
$C_8H_9O_4N_3$ requires N = 19·9 per cent.

3:5-*Dinitro-o-4-xylidine* is readily soluble in the cold in chloroform, benzene, or ethyl acetate, and crystallises from ethyl alcohol in orange-red needles, melting at 143°.

The *acetyl* derivative, prepared by heating the nitroamine with a mixture of equal parts of acetic anhydride and acetic acid, crystallises from alcohol in transparent needles, melting at 223°:

0·1204 gave 16·8 c.c. N_2 (moist) at 19° and 768 mm. N=16·32.

$C_{10}H_{11}O_5N_3$ requires N=16·6 per cent.

The conversion of 3:5-dinitro-*o*-4-xylidine into 3:5-dinitro-*o*-xylene was carried out exactly as described in the case of 4:6-dinitro-*o*-3-xylidine (see p. 2349). The resulting substance crystallised from alcohol in needles, melting at 75°, nor was this melting point altered on admixture with pure 3:5-dinitro-*o*-xylene.

Nitration of 3-Nitroaceto-o-4-xylidide.

3-Nitroaceto-*o*-4-xylidide was prepared by reducing 3:4-dinitro-*o*-xylene with stannous chloride (compare this vol., p. 2342), and heating 2 grams of the resulting 3-nitro-*o*-4-xylidine with acetyl chloride for two hours. If the heating with acetyl chloride is continued for a longer period, a product of higher melting point, probably a diacetyl derivative, is produced. The excess of acetyl chloride was then evaporated, and the resulting viscid solid triturated with cold ethyl alcohol, when 2 grams of a clear, white solid were obtained, which crystallised from alcohol in stout, transparent needles, melting at 115° (compare Noelting, Braun, and Thesmar, *Ber.*, 1901, **34**, 2251).

One gram of 3-nitroaceto-*o*-4-xylidide was dissolved in 5 c.c. of concentrated sulphuric acid, cooled in a freezing mixture, and 15 c.c. of a mixture of one part of nitric acid (D 1·42) and two parts of concentrated sulphuric acid added, so that the temperature remained below −3°. The whole was allowed to remain at this temperature for two hours, poured on ice, filtered, the residue washed with a little ether, and crystallised from alcohol, when 9·4 grams of pure 3:5-dinitroaceto-*o*-4-xylidide were obtained.

The nitration was also carried out with fuming nitric acid and sulphuric acid, and also with nitric acid (D 1·5 and 1·42) alone; the former gave rise to the same dinitroaceto-*o*-xylidide, but in smaller yield, and with nitric acid only resinous products were obtained.

Nitration of Aceto-o-4-xylidide.

(*a*) *With Fuming Nitric Acid.*—One gram of aceto-*o*-4-xylidide was gradually added to 10 c.c. of fuming nitric acid, the temperature being maintained below −5°. The whole was poured on ice,

and the precipitated solid (1·1 grams) crystallised from alcohol, when pure 3:5-dinitroaceto-*o*-4-xylidide, melting at 223°, was obtained.

(*b*) *With Fuming Nitric Acid and Sulphuric Acid.*—Five grams of aceto-*o*-4-xylidide were dissolved in 30 c.c. of concentrated sulphuric acid, cooled in a freezing mixture, and 45 c.c. of a mixture of one volume of nitric acid (D 1·5) and two volumes of sulphuric acid gradually added. The whole was poured on ice, the solid collected and crystallised from alcohol, when 5·1 grams of a substance melting at 170—171° were obtained:

0·1030 gave 14·8 c.c. N_2 (moist) at 20° and 754 mm. N=16·30.

$C_{10}H_{11}O_5N_3$ requires N=16·60 per cent.

5:6(3:4)-*Dinitroaceto*-o-4-*xylidide* crystallises from alcohol in fine, white needles melting at 173°. It was saponified by heating to 110° with ten times its weight of concentrated sulphuric acid for ten minutes, poured on ice, and the precipitate crystallised from alcohol:

0·1036 gave 18·2 c.c. N_2 (moist) at 22° and 753 mm. N=19·72.

$C_8H_9O_4N_3$ requires N=19·9 per cent.

5:6(3:4)-*Dinitro*-o-4-*xylidine* is only very moderately soluble in ethyl alcohol, benzene, or chloroform, and crystallises from acetone in deep orange-red needles, melting at 212°. When the amino-group was removed from this dinitroamine by the process described on p. 2349, it gave 3:4-dinitro-*o*-xylene, melting at 82°.

(*c*) *With Nitric Acid* (D 1·42) *and Sulphuric Acid.*—When aceto-*o*-4-xylidide was nitrated by adding to its solution in concentrated sulphuric acid a mixture of nitric acid (D 1·42) and concentrated sulphuric acid, it gave 6(3)-nitroaceto-*o*-4-xylidide, melting at 210°, and previously described by Noelting. The latter substance on treatment with fuming nitric acid was converted in good yield into 5:6(3:4)-dinitroaceto-*o*-4-xylidide, melting at 173°.

Nitration of 5-*Nitroaceto*-o-3-*xylidide.*

(*a*) *With Fuming Nitric Acid.*—5-Nitro-*o*-3-xylidine (m. p. 111°) was prepared by reducing 3:5-dinitro-*o*-xylene with stannous chloride (compare this vol., p. 2342). The acetyl derivative melting at 230° (compare Noelting, Braun, and Thesmar, *Ber.*, 1901, **34**, 2247) is best prepared by dissolving the amine in five times its weight of benzene, adding a solution of acetic anhydride (in amount equal to that of the amine taken) in benzene, warming for a minute or two, when the whole becomes semi-solid, and crystallising the solid from alcohol. Twenty-four c.c. of fuming nitric acid were gradually added to 2 grams of 5-nitroaceto-*o*-3-xylidide surrounded by a freezing mixture, the whole allowed to remain for one and

a-half to two hours at 8—10°, poured into ice-water, the precipitate washed with a little ether, and crystallised from alcohol:

0·1048 gave 15·2 c.c. N_2 (moist) at 22° and 767 mm. N = 16·58.
$C_{10}H_{11}O_5N_3$ requires N = 16·6 per cent.

4 : 5-*Dinitroaceto*-o-3-*xylidide* is very readily soluble in acetone and ethyl acetate, moderately so in hot alcohol or benzene, and crystallises from alcohol in colourless needles, melting at 225°. It was hydrolysed by heating to 90° for five minutes with ten times its weight of concentrated sulphuric acid, poured into water, and the precipitate crystallised from alcohol:

0·1010 gave 17·3 c.c. N_2 (moist) at 20° and 769 mm. N = 19·83.
$C_8H_9O_4N_3$ requires N = 19·9 per cent.

4 : 5-*Dinitro*-o-3-*xylidine* is readily soluble in the cold in acetone or ethyl acetate, readily so on warming in benzene or chloroform, and crystallises from alcohol in radiating clusters of orange needles, melting at 143°. On removal of the amino-group by the method already indicated, 4 : 5-dinitro-*o*-xylene, melting at 115°, was obtained.

(*b*) *With Fuming Nitric Acid and Sulphuric Acid.*—Six grams of 5-nitroaceto-*o*-3-xylidide were dissolved in 30 c.c. of concentrated sulphuric acid, and 90 c.c. of a mixture of one volume of fuming nitric acid and two volumes of sulphuric acid gradually added, allowed to remain at 8—10° for two hours, poured on ice, and the precipitate crystallised from a mixture of four parts of benzene and one part of acetone:

0·1012 gave 14·8 c.c. N_2 (moist) at 24° and 758 mm. N = 16·44.
$C_{10}H_{11}O_5N_3$ requires N = 16·6 per cent.

5 : 6-*Dinitroaceto*-o-3-*xylidide* is readily soluble in alcohol, acetone, or ethyl acetate, and crystallises from the above-mentioned mixture of solvents in white plates, melting at 180°. It was hydrolysed by heating with ten times its weight of concentrated sulphuric acid for twenty minutes at 110—115°, and the product crystallised from alcohol and analysed:

0·1114 gave 19·7 c.c. N_2 (moist) at 24° and 756 mm. N = 19·71.
$C_8H_9O_4N_3$ requires N = 19·90 per cent.

5 : 6-*Dinitro*-o-3-*xylidine* is readily soluble in the cold in ethyl acetate or acetone, and crystallises from alcohol in deep yellow needles, melting at 172°. It is soluble in concentrated hydrochloric acid to form a colourless solution, which deposits tabular crystals of a very unstable hydrochloride. This is the only dinitro-*o*-xylidine described in this communication which shows any tendency to form salts.

RESEARCH LABORATORY, PHARMACEUTICAL SOCIETY,
17, BLOOMSBURY SQUARE, W.C.


MARCELIN BERTHELOT
LA SYNTHESE CHIMIQUE
LA SCIENCE GUIDE L'HUMANITE


POUR LA PATRIE ET LA VERITE 1901

BERTHELOT MEMORIAL LECTURE.

DELIVERED ON NOVEMBER 23RD, 1911.

By HAROLD BAILY DIXON, M.A., Ph.D., F.R.S., Past-President of the Chemical Society.

(1) *His Career.*

IN this age of extreme specialisation, the life and work of Berthelot teach the world the much-needed lesson that men of science are not necessarily men of one idea, but may be great, not only as experimenters, but great also as thinkers and as citizens. On all that he turned his mind to—and few things were foreign to his interest—Berthelot brought to bear, not only an exact scientific method and an exquisite clearness of statement, but an imagination as foreseeing as it was comprehensive, a patriotism as pure as it was enlightened. In the work of his life—whether as a philosopher or as a Cabinet Minister—Berthelot looked to Science as his guide. He believed in science as an illuminating and humanising force; he believed that in science lay the secret of the progress of France and of mankind. To pursue science was to ensure progress; science was to him a mission, a recreation, a religion. "To the end of my life," he wrote half-sadly to Renan (in 1892), "I shall be the dupe of this desire for progress which you so wisely relegate to the sphere of illusions." But of the reality of the progress achieved by Berthelot no chemist can doubt. In the realm of industry alone what tempting offers were made to him for a monopoly of his synthetic processes in organic chemistry. But Berthelot never bargained with or patented his discoveries. "The man of science," he declared, "should make the possession of Truth his only riches." Not that Berthelot considered the applications of science beneath him; on the contrary, he believed that science should be pursued largely by reason of its service to mankind. "Science has a double aim," he wrote, "an ideal aim which is the search for pure truth, and a positive and human aim which is the good of man and the development of civilisation."

Pierre Eugène Marcelin Berthelot* was born in the heart of the old Paris, in the Place de Grève—now Haussmannised out of recognition into the Place de l'Hôtel de Ville—on October 25th, 1827.

* I am indebted to the kindness of Berthelot's son—Prof. Daniel Berthelot—for exact names and dates, and also for much other valuable information. I desire also to express my obligation to my old student, Mr. A. S. Robinson, for making me a *précis* of Berthelot's papers.

He died in Paris, March 18th, 1907. As he was born and bred, so he lived and died a Parisian.

Through his father, Dr. Jacques Martin Berthelot, the son inherited his scrupulous regard for duty, his serious love for science, his liberal instincts, and his philosophic outlook on life; through his mother, Ernestine Sophie Claudine Béard, he inherited his ardent and responsive nature, his amazing industry, his versatility, and his curiosity. From the Place de Grève his family moved to a house near by in the narrow Rue des Ecrivains, just opposite the Tour Sainte-Jacques. The somewhat delicate and highly-strung boy grew up in sight of those royal ceremonials—the Corpus Christi processions from the Tuileries to Notre Dame—when people in the street were obliged to kneel, under penalty of sacrilege, as the procession passed. As a child the roar of the revolution must have sounded in his ears, for his father's house overlooked the scene of many of those deeds of violence that marked the popular upheaval against the Ordinances of the 25th of July (1830). Then, as again in the later revolutions, the house became a hospital equally for Royalist and for Republican, for Dr. Berthelot made no distinction between his patients, however much his sympathy went out to the suffering people.

Even from the age of ten, Berthelot tells us, he began to ponder on the problems of life, and was troubled by the insecurity of the future. Nevertheless, he was an industrious and brilliant scholar, and made rapid progress at the school he attended—the Collège Henri IV. Sixty years later at the Jubilee Celebration, M. Fouqué, the President of the Académie des Sciences, bore striking testimony to Berthelot's gifts as a boy. "Everyone admires in you your power of work, your spirit of invention, your logic of ideas, your grasp of memory, your skill in experiment. . . . I affirm that these precious gifts you already possessed in the germ when you were still a simple schoolboy. More than half a century ago we sat side by side on the benches of the mathematical class in the Collège Henri IV.; a close comradeship grew up between us. My recollections bring back with pleasure the long talks we had on every kind of question. . . . I still see myself in discussion with you on the muddy road that led to your house at the foot of the Tower of Saint-Jacques. There I met the kindest greeting from your father, and then we climbed to your attic and resumed our interrupted argument—our only distraction being the swallows that built among the sculptures of the old tower."

At the end of his school course in 1846 he took the highest prize in competition with all the best students from the lycées of Paris—

the "prix d'honneur de philosophie." To his sound classical education he attached great value, and his love of ancient literature lasted through life. Two old editions of Lucretius and of Tacitus, preserved from his schooldays, were his constant companions whenever he left Paris. He quoted Horace familiarly, and he has told us that he soon recovered his Greek when he began to decipher the Alexandrine MSS. on Alchemy.

His school studies over, he made up his mind to pursue natural science as a career, and he even mapped out a programme for the methodical study of the principles of *all* branches of science in what he afterwards called the "naïve confidence of youth." But, however much he may have had to curtail his educational ambition, he completed during the next few years a full medical course, he studied chemistry in the laboratory of Pelouze, and passed the University examinations for Bachelier and Licencié-ès-Sciences. To carry out this programme he took a small lodging in the Rue de l'Abbé-de-l'Epée, and attended the school of M. Crouzet. In this school happened that fortunate meeting between Berthelot and Ernest Renan—the beginning of a friendship which became from that day a principal element in the lives of both. Renan, then twenty-two, had renounced his clerical orders, and retired from Saint-Sulpice. Lonely and depressed by his mental struggles, he had become an assistant master in the school, but could not shake off his melancholy. Berthelot spoke to him, the talk became intimate, something in each ardent nature was touched and responded, and the two were drawn together until soul reacted with soul like acid and alkali. "Our friendship," wrote Renan, "was something analogous to that of the two eyes when they fix upon the same object, and from the two images there results a single impression in the brain." Renan and Berthelot would take long walks together, and on Sundays would visit Neuilly, then in the country, where Berthelot's parents had taken a house, and always they discussed the eternal problems that torture the human mind. One day Renan called his young friend a "Revolutionist." But Berthelot had one sure faith, built on the ruins of other beliefs. "I a Revolutionist!" he cried, "clear your mind of that notion; call me rather an 'Evolutionist.'" We must remember that this was said a decade before Darwin gave us the "Origin of Species."

The ideas resulting from their stimulating intercourse took different shapes in the two minds, and though Renan admitted his indebtedness to Berthelot, it is impossible for us, as it was for them, to separate what was due to each. On the monument of Berthelot

which is to be placed in the Gardens of the Luxembourg, the sculptor, Saint Marceau, has introduced the face of Renan as a memorial of one of the most notable friendships of our time.

Under Pelouze the experimental skill of the young chemist rapidly developed, and in 1850 he presented his first paper to the Academy of Sciences—"On a simple method of demonstrating the liquefaction of gases." He showed how the gases chlorine, ammonia, and carbon dioxide could be liquefied in the capillary end of a glass tube by the expansion of mercury filling the body of the tube. When oxygen and nitric oxide showed no sign of liquefaction under pressures of 700 to 800 atmospheres he rightly concluded that under certain conditions of temperature it was not possible to liquefy gases by pressure alone. A second paper appeared in the same year, and in January, 1851, Berthelot received his first appointment, that of lecture-assistant to Balard, the discoverer of bromine, then Professor of Chemistry in the Collège de France. Unluckily the stipend was not a living wage—800 francs (£32) a year—and to earn a living Berthelot had to give private lessons. Luckily the official duties of the post were not heavy, and the resources of the laboratory were placed freely at his disposal by Balard, who in proposing him for the post wrote: "Everything allows us to hope that M. Berthelot will know how to utilise for the advancement of science the position I ask for him." In three years from his appointment Berthelot had obtained his doctorate by his remarkable thesis, "On the combinations of glycerine with acids, and on the synthesis of the immediate principles of animal fats." A year later he began to publish his work on the sugars, and the same year (1855) made the memorable syntheses of ethyl alcohol from ethylene, and of formic acid from carbon monoxide, which revolutionised the accepted ideas on the formation of organic compounds. Then followed in quick succession researches on the synthesis of hydrocarbons, of methyl alcohol, and of oxalic acid. After eight years' brilliant work, Berthelot was appointed Professor in the École Supérieur de Pharmacie, where he lectured, but he continued to act as assistant and to research in the Collège de France. This was the first public recognition of his discoveries. Early in the following year (1860) this Society honoured itself and him by electing him a Foreign Member. At the invitation of Alexander Williamson, then President, Berthelot lectured before the Chemical Society "On the synthesis of organic substances," on June 4th, 1863. It is pleasant to think that our Chemical Society set, rather than followed, the fashion.

With the appearance of his first book, "Organic Chemistry founded on Synthesis" (1860), the fame of Berthelot quickly spread.

The Jecker Prize was awarded to him in 1861 by the Academy of Sciences. The professors of the Collège de France, headed by Balard, petitioned the Minister of Public Instruction to found a Chair for Berthelot, and this movement resulted in his being appointed to a Professorship in the College in 1861, and finally (in August, 1865) in the formation of a special Chair of Organic Chemistry, which Berthelot held until his death. But though his early academic promotion was slow, honours came thickly to him in his middle age. The French Academy of Medicine elected him a member in 1863; he was elected to the Academy of Sciences in 1873, and of this body he succeeded Pasteur as Perpetual Secretary in 1889. In 1900 he became one of the forty French Academicians.

I cannot attempt any enumeration of the various learned societies of which he became an honorary fellow; I will only mention that he was elected a foreign fellow of our Royal Society in 1877, and that a Davy Medal was awarded in duplicate to him and to his friendly rival in thermochemistry, Julius Thomsen, in 1883, and that he received the Copley Medal, the highest distinction the Royal Society has to bestow, in 1900.

On his appointment to a Professorship in the Collège de France, Berthelot was enabled to fulfil his engagement to Mademoiselle Sophie Caroline Niaudet, niece of M. Louis Breguet, a French Swiss, whose family had been prosperous manufacturers of scientific instruments for many years, and who himself was the constructor of a well-known telegraph and induction coil. The story goes that the Berthelot and Breguet families had been intimate for some years, but Marcelin had not lifted his eyes to the beautiful Mademoiselle Sophie until one day accident brought them into collision on the Pont-Neuf. She was crossing the long bridge in front of Berthelot, and making her way with difficulty in the teeth of a strong wind, when a stronger gust catching her skirt and Tuscan hat blew Mademoiselle round into the arms of her future husband.

They were married on May 10th, 1861. Never was a happier match, or a more devoted family than Berthelot's. Madame Berthelot was endowed above most women with grace, with tact, and with sympathy; she brought into his life that great gift of serenity which Berthelot regretted he had not inherited from his mother. Well might he have appreciated our homely English saying, "It's an ill wind that blows nobody any good."

Busy in his laboratory by day and in his study by night, Berthelot took little part in public life under the imperial régime until the overthrow of Louis Napoleon and the siege of Paris in 1870. Then he threw himself whole-heartedly into the work of resisting the

invaders, and as president of the Scientific Committee of National Defence superintended the manufacture of explosives to be used against the enemy. After the war Berthelot continued the study of explosives, to which he applied all his experimental skill and the knowledge he had acquired in his thermochemical researches. In collaboration with Vieille he began a systematic investigation of the phenomena of explosions, which finally resulted, not only in the invention of a powder that gave to French arms for some years a remarkable superiority, but in the addition to science of a new chemical constant—*l'onde explosive.*

His work on the combination of nitrogen with organic bodies under the influence of the silent electric discharge turned his attention to the fixation of nitrogen by plants in the soil; in 1884 a laboratory was built for him on the heights of Meudon, and here he devoted himself every summer to problems of vegetable chemistry.

Determined to take his share in the government of his country, he was elected a Permanent Senator in 1881, and in 1886 became Minister of Public Instruction in the Cabinet of M. Goblet. Here he found the opportunity of impressing on his generation his strong convictions on the educative and liberalising power of science. But he was no advocate of an illiterate mechanical training; he held firmly that science should be taught on the sound basis of a literary culture. It was in this spirit that he met the demand for "technical education" which swept over Europe. Industry demands two things, according to Berthelot: capable directors and competent workers. To be capable the director must be a judge of men and a judge of things; he must be trained in literature, history, and science; the high school and the university will prepare him for his business. To be competent the worker must be intelligent and skilful; the elementary school and the workshop will fit him for his job. Berthelot saw no need for ordinary technical schools—except as evening schools to help the workman. Can we yet say that Berthelot was wrong? At all events, he knew what he wanted, and he helped France to get it.

In 1895 Berthelot accepted the Portfolio of Foreign Affairs in the Bourgeois Cabinet. In this difficult post he had to negotiate the Anglo-French treaty dealing with the status and boundaries of Siam, which found herself in the uncomfortable position of "buffer" state between the French in Annam and the English in Burmah. Berthelot did not feel the duties of the Foreign Office congenial, and he resigned shortly after signing the treaty with Great Britain. But this, I think, we can say—that as a politician he had a sincere regard for England, and had he continued to guide the foreign relations of France the *Entente*, that has happily smoothed away

so many difficulties between the two nations, might have blossomed a decade earlier.

That Berthelot was a man of peace is evident from his book, "Science et Libre Pensée." It contains a strong plea for international arbitration. Of his other books mention must be made of his studies of the Greek and Arabian alchemistic writings. In 1869 Berthelot visited Egypt, where his imagination was struck with the early records of chemical and metallurgical experiments and ideas. He returned to this subject later, and followed it up with his characteristic eagerness. By his influence he obtained the publication of many rare manuscripts on alchemy, which he edited in collaboration with M. Ruelle, "Collection des Alchimistes Grecs," and with MM. Duval and Houdas, "La Chimie au Moyen-Age."

Few more interesting chemical papers have ever been published than the hundred and one preparations and recipes comprised in the Papyrus of Leyden translated by Berthelot. They reveal some of the methods of the Egyptian priesthood, who were the holders of the secrets of chemistry. How pithily is described the conversion of a copper vessel into a beautiful vase of gold (by rubbing it with gold amalgam and heating)—a vase which will stand the regular test of the touch-stone! With what cynical pleasure Berthelot remarks that such a fraud was no doubt quite natural, and even commendable in the eyes of a priest!

In 1880 it was my great privilege to be introduced to Berthelot in his laboratory at the Collège de France by Sainte-Claire Deville and Alexander Williamson. I had just been showing for the first time non-explosive mixtures of dried carbon monoxide and oxygen at the British Association Meeting at Swansea. Deville was enthusiastic over the discovery, since it upset one of our cherished ideas; but Berthelot was more philosophical. Carbon monoxide was a gas, he said, "a little capricious" in its ways. One must repeat and again repeat such experiments. Most sound advice! I had, by the way, been repeating these experiments for four years before I published them; and it was in "again repeating" them that, all unconsciously, I struck across one line of Berthelot's own work—the measurement of the rate of explosion in gases.

But except for this natural attitude of philosophic doubt Berthelot was kindness itself. We were taken to his home in the Institute, and were entertained by Madame Berthelot, whose silver hair heightened the saint-like beauty of her face. Berthelot was full of fire and quick replies. When Williamson rallied him on the rapidity with which his memoirs appeared, Berthelot replied, "Ah! you English are too cautious, too frightened of committing your-

selves; what is worth doing is worth publishing!" It was perhaps characteristic of him that an hour before he had given me the opposite and better advice.

Those who met Berthelot in his prime could not but be struck with the intellectual sincerity and the intense enthusiasm of the man. The broad forehead, the brilliant, blue eyes, the clean-cut features, and the thoughtful expression impressed all who saw him; while his musical voice and clear enunciation charmed the ear. It would be impossible to forget that first impression.

Students who attended his lectures speak in the highest terms of the inspiration they drew from his teaching. He gave of his best, and delighted to show his audience the new experiments he was engaged upon. But it was when he forgot the immediate experiment in hand, and began to think aloud, that the inspiration was highest. Here truly was science "in the making."

(2) *His Scientific Work.*

In considering the amazing output of scientific work we owe to Berthelot, it would be useless to enumerate, and hopeless to discuss individual memoirs. Luckily they can be grouped into well-marked divisions, for Berthelot always followed up a train of thought until some logical explanation was reached that satisfied his mind. Then some idea suggested by the first research was followed up experimentally until another generalisation was reached, and other trains of thought could be pursued.

Study of Glycerine.—As soon as he was installed in Balard's laboratory in the Collège de France, Berthelot took up a line of research which led him on to discoveries of the highest interest. He began to study the modes of combination of glycerine with acids, and proved that it was an alcohol capable of combining with acids to form "etherial salts"—thus bearing out the views of Chevreul that fats were "compound ethers," and justifying the modern name "glycerol"; but he also showed that glycerol differed from ordinary alcohol by its ability to combine with three equivalents of an acid instead of with one, just as phosphoric acid differs from nitric acid in combining with three equivalents of a base. By what seems a curious mental slip Berthelot likened the three classes of esters formed by glycerol to ortho-, para-, and meta-phosphates, instead of to their true analogues, the three salts of ortho-phosphoric acid. Wurtz not only made the correction, but by his synthesis of glycol—the "diatomic" intermediate between the "monatomic" alcohol and the "triatomic" glycerol—confirmed the importance of Berthelot's discovery. The work of Berthelot and Wurtz on the

polyatomic alcohols must rank in importance with that of Liebig on the organic polybasic acids. I think, also, it is clear that the analogies shown by alcohols to inorganic bases—and I may specially mention the analogy between glycerol and bismuth hydroxide pointed out by Odling—led to the general adoption of the idea of valency which had been given to chemistry by Edward Frankland. The proof that glycerol is an alcohol led Berthelot to prepare and examine many other bodies of a like nature. We are indebted to Berthelot for a considerable number on the list of substances recognised as alcohols, and we constantly employ his method of acetylisation as the means of recognition.

Synthesis of Organic Substances.—I can only make a passing mention of very few of the many compounds of glycerol prepared by Berthelot by submitting it to the action of acids. Hydriodic acid, he found, yielded two substances, *iso*propyl iodide and allyl iodide; from the latter he made for the first time artificial oil of mustard.

The curious reducing power of hydriodic acid, especially at a high temperature, he afterwards made good use of in reducing benzene- to hexane-derivatives (1867). But the most stimulating thing to Berthelot's mind was the discovery that glycerol would combine, if time were given it, with all sorts of different acids, producing new fatty bodies, and that one could predict the formation of an endless number of new substances through a "creative power greater than that realised in nature." This idea, once planted in his mind, grew apace. He sought and found methods for preparing the simpler types of organic compounds, and from these to pass on to the higher and more complicated. To appreciate the boldness of Berthelot's conceptions we must remember the firm conviction that chemists held throughout the first half of the last century, that there was a gulf fixed between inorganic and organic substances; the chemist might build up, or synthesise, inorganic salts, but he could only break down, or analyse, the substances created in plants and animals by the "vital force." This gulf had not been really passed in the eyes of most chemists by the synthesis of urea by Wöhler or the formation of acetic and propionic acids from their nitriles by Kolbe and Frankland, for the cyanides from which these substances were formed were regarded as organic products themselves.

Berthelot's first success on his new path came in 1855. He shook up pure sulphuric acid in a large globe holding 32 litres of ethylene gas until 30 litres of the gas had been absorbed. The liquid was then mixed with water and distilled. The liquid coming over was dried and redistilled until 45 grams of a liquid having all the

properties of pure alcohol were obtained. But the original ethylene had itself been obtained from alcohol—so the synthesis might be said to be contaminated at its source. Berthelot next prepared ethylene iodide from coal gas, and from this prepared a sample of ethylene, which he treated as before. It yielded alcohol, which was thus made for the first time without fermentation.

Now since ethyl alcohol on heating with sulphuric acid yields ethylene and water, and formic acid on heating with sulphuric acid yields carbon monoxide and water, if the first process can be reversed, it might be predicted that the second would also:

$$C_2H_6O = C_2H_4 + H_2O.$$
$$CH_2O_2 = CO + H_2O.$$

Berthelot placed 10 grams of potash in a half-litre flask, which he filled with carbon monoxide, sealed, and heated for three days on a water-bath. When the flask was opened under mercury the gas was found to be completely absorbed; on dissolving the potash salt in dilute sulphuric acid and distilling, Berthelot obtained a distillate of formic acid.

In the following year (1856) a more difficult synthesis was effected —that of marsh gas, together with ethylene and acetylene. Formic acid on heating yields all its carbon as carbon monoxide and its hydrogen as water; but if there is present a strong base, which might cling to some of the carbon, a substance containing carbon and hydrogen might be evolved. Berthelot prepared formic acid on a large scale from carbon monoxide, combined it with baryta, and distilled the barium formate at a red heat. He condensed a small amount of liquid, caught the unsaturated hydrocarbons in bromine, and collected the marsh gas over water. The unsaturated hydrocarbons were ethylene and propylene. On decomposing their bromides by means of water and copper foil in thick glass tubes at 275°, Berthelot regenerated the ethylene and propylene, and found about 10 per cent. of acetylene—the result of a secondary action. From this ethylene he again prepared pure alcohol.

Berthelot's next starting point was carbon disulphide. If carbon disulphide were heated with a metal capable of combining with the sulphur, while at the same time hydrogen were liberated in contact with the nascent carbon, the two might combine to form a hydrocarbon. Passing hydrogen sulphide and carbon disulphide vapour through a broad tube packed with copper turnings freshly reduced and heated to a dull red heat, Berthelot condensed a trace of naphthalene, and collected ethylene in bromine and marsh gas over water. Iron acted in the same way as copper, and hydrogen phosphide and steam could be used instead of hydrogen sulphide.

Berthelot regenerated the ethylene as before (finding acetylene produced), and prepared alcohol from it. One cannot help feeling in reading Berthelot's account of this experiment that in his mind the ethylene (with its resulting alcohol) was more important than the marsh gas. But a year later Berthelot chlorinated marsh gas in diffused daylight, separated the methyl chloride from the residual marsh gas and higher chlorides by solution in anhydrous acetic acid, and prepared methyl alcohol from the chloride.

Just as Berthelot had got ethyl alcohol from ethylene and sulphuric acid, so he obtained propyl alcohol from propylene and sulphuric acid. The propylene was prepared from the propyl iodide obtained from glycerol and phosphorus iodide. Again he showed that the higher olefines could be combined with hydrogen chloride and the chlorides turned into the corresponding alcohols—a general method by which he prepared many alcohols; and *vice versâ*, by abstracting the elements of water the olefines could be prepared from the alcohols. Again, as barium formate yielded on distillation several hydrocarbons, so might the acetate of sodium yield other hydrocarbons than marsh gas. Berthelot found that it yielded higher olefines as well, namely, propylene, butylene, and amylene.

But among the most memorable of Berthelot's syntheses was the direct combination of hydrogen and carbon in the electric arc to form acetylene (1862), and the condensation of acetylene into benzene (1866); thus the barrier between inorganic and organic chemistry was broken down at all points, and Berthelot's disciples could exclaim with justice: "There is but one chemistry, and Berthelot is its prophet."

In working on acetylene Berthelot investigated the properties of the acetylides of silver and copper. This work led him in 1866 to make the suggestion that the mineral oils found in the earth might have been formed from acetylene produced by the action of water and carbonic acid on the acetylides of the alkali metals. By reducing the carbonaceous matter found in meteorites he produced some liquid petroleum.

Action of Heat on Hydrocarbons.—Berthelot's work on the hydrocarbons included a study of the mode in which these bodies behave at a red heat. A hydrocarbon, he says, is not directly resolved into its elements, but either polymerises (for example, acetylene into benzene) or by a condensation of two or more molecules forms a denser hydrocarbon with elimination of hydrogen; thus marsh gas gives mainly acetylene and hydrogen, ethane yields ethylene and hydrogen, while ethylene yields mainly acetylene and hydrogen. Acetylene itself is not resolved into its elements, but polymerises,

or condenses with hydrogen or other hydrocarbons into compounds of great density—naphthalene, anthracene, etc. When carbon is finally separated, it is therefore not a simple molecule, but in the form of a highly complex group of atoms corresponding with the dense hydrocarbons yielding it. This attractive theory of Berthelot has not, however, been fully borne out by later work. Sir Edward Thorpe showed that the decomposition of a paraffin (under heat and pressure) gave rise to the formation of an olefine and a lower paraffin; and Haber showed that *n*-hexane gave methane and amylene, but confirmed Berthelot's observation that benzene condensed to diphenyl with loss of hydrogen. Bone and his colleagues have shown that methane is formed directly from its elements between 1000° and 1200°, and breaks up again into carbon and hydrogen without forming acetylene. Ethylene, on the other hand, gives acetylene, which itself can either recombine with hydrogen or break down into carbon and hydrogen.

Action of Mass.—The observation made by Berthelot that time was required for the union of glycerol with acids led him, in conjunction with his pupil, Péan de St. Gilles, to investigate the course of the reaction between alcohols and acids, especially that between ethyl alcohol and acetic acid. Here, again, Berthelot was a pioneer in a subject that had hardly been touched experimentally. He found that when equivalent amounts of alcohol and acid are brought together, the reaction proceeds slowly (at a rate depending on the temperature) until a limit is reached, and that the same limit is reached when the corresponding amounts of ester and water are brought together. "An equilibrium is established between the affinity of the acid for the alcohol, which tends to unite them, and the inverse affinity of the water for the neutral ether, which tends to regenerate the acid and the alcohol." We can put the result into an equation:

$$\frac{C_2H_3O_2{\cdot}C_2H_5 \times H_2O}{C_2H_4O_2 \times C_2H_6O} = 4.$$

It is clear, I think, that Berthelot regarded the equilibrium as a statical, and not as a dynamical, one; he did not see that the two opposite reactions were taking place at the same time; Guldberg and Waage recognised this, and used Berthelot's figures in illustration of their principle. Nevertheless, Berthelot and St. Gilles' memoirs form the starting points of much of the subsequent work on equilibrium and mass action. They showed the effect on the equilibrium of varying the amounts of one of the reacting substances; they showed that an increase of temperature or of concentration greatly shortened the time for the equilibrium to be

reached, although pressure alone had little effect. They suggested an equation for the determination of the velocity of a bimolecular reaction similar to that of Harcourt and Esson. Few researches indeed have been more fruitful in physical chemistry than those of Berthelot and St. Gilles.

Of other equilibrium problems Berthelot was the first to investigate the partition of a dissolved substance between two solvents. He showed, for instance, that when succinic acid is dissolved in ether and water, the coefficient of distribution is constant whatever the amounts dissolved; but other substances showed a variation with concentration, an anomaly explained by Nernst in 1891 as due to a difference of the molecular aggregation of the substance in the two solvents. In 1875 Berthelot studied the partition of acids between several bases in solution.

Thermochemistry.—Berthelot's great work on thermochemistry was begun in 1863, and was continued until 1879, when he published the two volumes entitled, "Mecanique Chimique fondée sur la Thermochimie." This and his later book, "Thermochimie, Données et Lois numériques," constitute a monument of elaborate experiment and calculation, which men of science rank alongside the "Thermochemische Untersuchungen," the life-work of Julius Thomsen. It is not at all to the disadvantage of Chemistry that the Frenchman and Dane worked in rivalry. When we want to know the heat of formation of any compound we look up the two authors, and if they agree we are entirely satisfied. I think each respected the other's work. I can point to an instance—the heat of formation of ammonia—where Thomsen corrected his first result, and to another—the heat of formation of ethane—where Berthelot corrected his; in each case as the result of the other's work. They both put forward a theorem, though not quite in the same terms, that every action of a purely chemical nature gives out heat and produces the result that is accompanied with the maximum evolution of heat. Berthelot defended with great skill his "principle of maximum work"; it required the genius of Helmholtz and Boltzmann to prove that the principle required that the heat of reaction should be independent of the temperature, and was only strictly true at absolute zero. But although these limitations must be accepted, and Berthelot finally accepted them, the "law" is nevertheless a useful guide which is often appealed to. Was not Deacon inspired by Berthelot's ideas when he sought and finally found a practical method of liberating chlorine from hydrochloric acid by the oxygen of the air?

Much of the apparatus devised by Berthelot for his thermo-

chemical determinations has come into general use; in particular, I may mention his "calorimetric bomb" for combustions in oxygen under pressure.

Explosions.—Berthelot's experiences in the war led to his systematic work on explosives and on the theory of explosions. In conjunction with Vieille he studied the rapidity of combustion and the heat of reaction of various explosives. In July, 1881, he published his first short paper on the explosion-wave in gases. He states that he would not have published it had not MM. Mallard and Le Chatelier sent him their memoir on the same subject, which they had attacked by a different method. It is a curious coincidence that a few months before I had myself begun to measure the rate of explosion of carbon monoxide and oxygen with different quantities of water-vapour, and found that the accepted rate was altogether too slow.

Berthelot's first paper contains the germ of his theory—the identity of the rate of explosion with the mean velocity of the molecules formed in the reaction before any heat had been lost. Other papers quickly followed. Berthelot made the important discovery that the rate of explosion rapidly increased from the point of origin until it reached a maximum which remained constant, however long the column of gases might be. This maximum Berthelot stated to be independent of the pressure of the gases, of the material of the tube, and of its diameter above a small limit. The rate of explosion thus forms a new physico-chemical constant, having important theoretical and practical bearings. The name "l'onde explosive" was given by Berthelot to the flame when propagated through an explosive mixture of gases at the maximum velocity, and this velocity could be predicted if the heat of combination and the density and specific heat of the products were known. For instance, the total heat given out when hydrogen and oxygen combine is known. If this heat is contained in the steam produced, its temperature may be calculated if its heat capacity be known; and if the temperature of the steam be known, the mean velocity with which the molecules must be moving can be calculated. Now Berthelot supposed that the heat is all contained in the steam produced. He assumed that the heat capacity of steam was the same as the sum of those of its constituents; and he supposed, moreover, that the steam was heated at constant pressure. Making these assumptions, he calculated out the theoretical mean velocity of the products of combustion of various mixtures, and found a close accordance between these numbers and the explosion rates of the same mixtures. He concluded that the explosion-wave was propagated by the impact of the products of combustion of one layer

upon the unburnt gases in the next layer, and so on to the end of the tube at the rate of movement of the products of combustion themselves. If this theory be true, it accounts, not only for the extreme rapidity of explosion of gaseous mixtures, and gives the means of calculating the maximum velocity obtainable with any mixture of gases, but it also affords information on the specific heats of gases at very high temperatures, and explains the phenomena of detonation whether of gases or of solid or liquid explosives.

Table I shows the explosion rates found by Berthelot, compared with the theoretical velocity of the products of combustion:

TABLE I.

Gaseous mixture.		Velocity in metres per second. Calculated.	Found.
Hydrogen and oxygen	$H_2 + O$	2830	2810
Hydrogen and nitrous oxide	$H_2 + N_2O$	2250	2284
Carbon monoxide and oxygen	$CO + O$	1940	1090
Carbon monoxide and nitrous oxide	$CO + N_2O$	1897	1106
Marsh gas and oxygen	$CH_4 + O_4$	2427	2287
Ethylene and oxygen	$C_2H_4 + O_6$	2517	2210
Cyanogen and oxygen	$C_2N_2 + O_4$	2490	2195
Acetylene and oxygen	$C_2H_2 + O_5$	2660	2482

Two facts established by these experiments impressed on me the conviction that Berthelot might have found the true theory of explosions: first, the close coincidence between the rates of explosion of hydrogen (both with oxygen and nitrous oxide) and the calculated mean velocities of the products of combustion; and, secondly, the great discordance between the found and calculated rates for carbonic oxide with both oxygen and nitrous oxide, for I had previously discovered that pure carbon monoxide cannot be exploded either with pure oxygen or pure nitrous oxide. The discordance found by Berthelot was what I should have expected from my own experiments. Again Berthelot examined the effect of inert gases in damping down the velocity of the explosion-wave; for instance, on adding nitrogen to different explosive mixtures he found:

TABLE II.

Gaseous mixture.	Velocity in metres per second. Calculated.	Found.
$H_2 + O$	2831	2810
$H_2 + O + N_2$	1935	2121
$H_2 + O + 2N_2$	1820	1439
$CH_4 + 2O_2$	2427	2287
$CH_4 + 2O_2 + 2N_2$	2002	1858
$CH_4 + 2O_2 + 4N_2$	1744	1151
$C_2N_2 + 2O_2$	2490	2195
$C_2N_2 + 2O_2 + N_2$	2334	2044
$C_2N_2 + 2O_2 + 2N_2$	2152	1203

These experiments seemed to Berthelot to show that a small amount of inert gas does not prevent the propagation of the true explosion-wave, but damps it down according to its calculated effect. A large amount of inert gas, on the other hand, destroys the character of the explosion-wave—which must always be regarded as the "*maximum possible*" velocity.

In comparing the rates of explosion determined in his tube with those calculated from his formula, Berthelot, I think, was not justified in his argument that the specific heats of the gaseous products must be reckoned as at constant pressure, since the whole change took place in a closed tube. In the damping experiments with nitrogen he did not allow for the fact that with inert gases a longer run is required before the explosion-wave is set up, and he began to time the flame before it had acquired its maximum pace. In the cyanogen experiments he did not appreciate the fact that in the wave-front the carbon only burns to carbon monoxide. But in spite of these criticisms, which required years of work to establish, I have always thought it one of Berthelot's strokes of genius to identify the maximum velocity of the flame with the mean translational velocity of the molecules themselves, a conception which all later investigators have used in working out the propagation of an intense pressure-wave which preserves its type by being continually reproduced from point to point by the chemical action.

Fixation of Atmospheric Nitrogen.—In Berthelot's synthetic researches we find him using the silent electric discharge to cause nitrogen to enter into combination, for example, as in the direct formation of hydrocyanic acid from acetylene and nitrogen. This fixation of nitrogen led him to investigate its absorption by plants, and generally the action of electricity on vegetable growth in his laboratory at Meudon. Berthelot asserted that free nitrogen could be assimilated by plants, a statement that was vehemently opposed until Hellriegel proved that leguminous plants can take up nitrogen through the agency of bacteria. Berthelot was the first to point out that atmospheric nitrogen was fixed in the soil by micro-organisms, a new departure of supreme interest to agriculture. Among other developments of Berthelot's idea, Dr. E. J. Russell has recently shown how the fertility of a soil might be enormously increased by killing off the infusorial enemies of these bacteria. Four solid volumes, entitled, "La Chimie végétale et agricole," published in 1899, contain the record of Berthelot's work at Meudon.

Looking back at the enormous mass of experimental detail published by Berthelot I am astonished at the small percentage of

error that has been detected. The accuracy of his experiments is really marvellous. It is not in his experiments, but in his interpretation of them that Berthelot has to meet criticism. Although Berthelot was a rapid worker, he was a still more rapid thinker. Not once or twice, but almost throughout the range of his researches we see the theoretical conception outstripping the experiment. Sometimes deliberately, sometimes unconsciously, he chooses his experiments to illustrate his theory. It is a question of idiosyncracy; genius must work its own way. The nineteenth century praised Dalton for basing his Atomic Theory on the sure foundation of the Law of Multiple Proportions; the twentieth century knows that Dalton sought for cases of multiple proportion to support his preconceived theory of atoms.

Berthelot's imagination gives a distinction to all his work; his rapidity of generalisation fascinates us, and compels our interest. Can we say which is the better for knowledge—on the one hand, the dashing advance of an explorer into an unknown country, the rapid survey, the approximate location of a great lake and a great mountain range, and the publication of a fascinating sketch-map giving us the possible sources of a Nile or a Congo; or, on the other hand, the deliberate advance of a surveyor with his levels and theodolites? May it not with justice be maintained that had it not been for the pioneer and his map the surveyor would never have started at all? Berthelot might rightly claim that he had pointed out the trend of the country and the possibilities that lay that way, and had stimulated the curiosity of the exploring world. "For myself," he wrote, "I shall be happy if, in the development of science, some of my results are valued some day as the origin of the discoveries of the future." I believe this was no conventional phrase of self-depreciation, but an expression of his thought used in all sincerity.

Again, like other great men, Berthelot found it hard, even when the creatures of his thought had been proved to be "unemployables," to dismiss them from his service. I ventured just now to compare Berthelot's mode of thought with Dalton's. May we extend the parallelism further, and say that the intensity of conception in the mind of each was sometimes too strong to yield to facts? Dalton, firm in his conviction that different elements had atoms of different sizes (the very genesis of his theory), could see neither the relevancy of Gay-Lussac's Law of Volumes nor the beauty of Avogadro's explanation. For him the formula of water was always HO. Berthelot, equally firm in his conviction that in chemical reactions we are dealing with "equivalents," could see the force of Gay-Lussac's experiments, but not of Avogadro's argument. For him

the formula of water (the molecule occupying 2 volumes) was H^2O^2.

If we, then, as the result of the steady progress of experiment and thought, can see the limitations of Berthelot's vision, we can also, I hope, appreciate the brilliancy of the conceptions that guided his work, and the intensity of the stimulus given by his ideas to contemporary science.

(3) *The Last Phase.*

Berthelot enjoyed a wonderfully active and honoured old age. To celebrate his seventy-fifth birthday and the jubilee of his first appointment in the Collège de France, his colleagues inaugurated a great meeting of congratulation, and commissioned M. Chaplain to design a medal in his honour.

The Chamber of Deputies and the Senate declared that the occasion demanded a public ceremonial, in which the State should participate. Abroad, all the great societies passed resolutions congratulating Berthelot on his achievements, and sent delegates to present their felicitations in person. The meeting was held in the great hall of the Sorbonne on November 24th, 1901. Berthelot declined the procession and the military escort offered by the State, and went on foot to the hall. He was received by the President of the Republic. Then amid the acclamation of his colleagues, who thronged the hall, he heard perhaps for the first time from the mouths of his most distinguished contemporaries the deep veneration in which the world held his genius and his career. In acknowledging this great demonstration, Berthelot once more insisted on the humanising spirit of science. "It is not," he cried, "for the satisfaction of our private vanity that the world to-day pays homage to men of science. No! it is because it knows that the man of science really worthy of the name consecrates his life disinterestedly to the great work of our age—the amelioration of the lot of all, the rich and the happy, the poor and the suffering. It is this that my friend Chaplain has sought to express on the beautiful medal which the President of the Republic is to offer me. I know not if I have completely fulfilled the noble ideal the artist has drawn, but at least it has brought me strength to have made this the aim that has directed my life."

"*Pour la Patrie et la Vérité*"—the design was well chosen by Chaplain to sum up Berthelot's career.

Berthelot continued to work to the end. Although he ceased to lecture, he seldom passed a day without visiting his laboratory. There and in his home he found his happiness, for husband and wife seemed to grow nearer as the years went by. In his last months

he had the sorrow of losing a daughter and then a beloved grandson. The shock preyed on his wife, who developed heart disease. Berthelot, himself a victim to the same disease, watched assiduously at her bedside, and wasted his strength in his nightly vigils over her. A Sunday came when she seemed better, and Berthelot visited his laboratory at Meudon, where he was studying the effects of radium emanations on vegetation. On his work table there was found afterwards an alchemic manuscript from Morocco, written in Hebrew, which he was deciphering, for he had not forgotten the early lessons he had received from Renan.

He returned to find his wife failing, and they both knew the end was near. "What will become of him when I am no longer there?" were the last words she spoke to her daughter. Berthelot was alone with his wife when she died. He called his children, kissed the dead, walked into the next room, and threw himself upon a couch. One of his sons followed him, and hearing him sigh, ran to seize his hand. But the hand was lifeless: he had joined his beloved one.

The pagan poet whom Berthelot loved has perhaps made us feel most keenly the cry of the heart that cannot survive separation:

> "Ah! te meae si partem animae rapit
> Maturior vis, quid moror altera,
> Nec carus aeque nec superstes
> Integer? Ille dies utramque
>
> Ducet ruinam. Non ego perfidum
> Dixi sacramentum. Ibimus, ibimus
> Utcumque praecedes, supremum
> Carpere iter comites parati." *

The state procession and military escort which Berthelot had declined alive, were fitting attendants round the hearse that bore the bodies of husband and wife to honourable sepulchre in the Pantheon.

So passed away a great man, full of years and honour. To France and to Science he gave his life, and he was not without reward in the love and veneration of his countrymen. Happy the country that produces such genius; happier still the country that can appreciate and use it.

* At the request of the Publication Committee, I subjoin the English rendering of these stanzas I gave at the Lecture:

> "If Death, untimely, snatch away
> That half—ah! dearer half—my soul,
> Why should this other half delay?
> Could life be sweet no longer whole?
>
> The day that strikes thee strikes us both:
> Together, when thou goest, we go
> Sworn comrades ('tis no idle oath)
> To tread the last long path below."
>
> —*Horace* II. xvii.

4373

INDEX OF AUTHORS' NAMES.

TRANSACTIONS AND PROCEEDINGS. 1911.

(Marked T. and P. respectively.)

D.

R.

T.

INDEX OF SUBJECTS.

TRANSACTIONS AND PROCEEDINGS. 1911.

(Marked T. and P. respectively.)

Single organic compounds of known empirical formula will be found in the Formula Index, p. 2397.

B.

C.

P.

FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Simple metallic salts of acids are indexed under the respective acids.

Simple salts of bases (for example, hydrochlorides, platinichlorides, and picrates), when described for the purpose of further identifying the base, are indexed under the latter.

C_1 Group.

C_2 Group.

2 III

C_3 Group.

3 III

3 IV

C_4 Group.

4 III

4 IV

C_5 Group.

5 II

5 III

5 IV

C_6 Group.

6 II

6 III

6 IV

6 V

C_7 Group.

8 III

8 IV

C_9 Group.

9 II

9 III

9 IV

C_{10} Group.

10 II

10 III

10 IV

C_{11} Group.

11 II

11 III

11 IV

C_{12} Group.

12 II

12 III

13 III

13 IV

C_{14} Group.

14 II

14 III

14 IV

C_{15} Group.

15 IV

C_{16} Group.

16 II

16 III

16 IV

C_{17} Group.

17 III

17 IV

C_{18} Group.

18 III

18 IV

C_{19} Group.

19 III

20 IV

C_{21} Group.

21 III

C_{23} Group.

23 III

23 IV

C_{24} Group.

24 III

ERRATA.

VOL. LXXXIX (TRANS., 1906).

Page	Line	
1468	11 and 12	*for analysis read:*

0·2801 gave 0·6353 CO_2 and 0·1850 H_2O. C = 61·86 ; H = 7·33.
$C_{10}H_{14}O_2N_2$ requires C = 61·9 ; H = 7·2 per cent.

VOL. XCV (TRANS., 1909).

Page	Line	
1774	22*	*for* "C_1" *read* "Cs."

VOL. XCVII (TRANS., 1910).

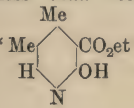
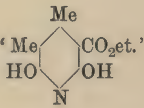
Page	Line	
2454	19*	*for* "a thousand" *read* "ten thousand."
2460		last number in 6th column of *viscosities* at 0° *for* "9703" *read* "8703," and fourth number of 7th column of *viscosities at* 10° *for* "8236" *read* "9236."
2462		Fig. 2 for "$\sqrt{\textit{normality}}$" read "$\sqrt[3]{\text{normality}}$."

VOL. XCIX (TRANS., 1911).

Page	Line	
451	20	*for* "acid" *read* "ester."
810	17*	,, "an acid salt, $C_6H_3O_6CuH$" *read* "a double salt, $C_6H_3O_6CuK$."
810	15*	,, "protocatechuate" *read* "pyrotartrate."
810	14*	,, "pyrotartrate and malate" *read* "protocatechuate and maleate."
810	13*	,, "C_2" *read* "C_4."
1263	5*	,, "Citraconic acid" *read* "Itaconic acid."
1269	22*	,, "*Special*" read "*Spatial.*"
1386	14*	,, "Paul" *read* "Pauly."

---

* From bottom.

Page	Line	
1545	4	*for* "39·4" *read* "32·4."
1662	10	*alter to* "In 1865, on Menschutkin's return to St. Petersburg, he presented his."
1835	15	*for* "RICHARD" *read* "ROBERTSHAW."
1852	14	*for* "RICHARD" *read* "ROBERTSHAW."
1907	16	*delete* "normal."
1909	5*	*insert* "$\rightleftharpoons$" in equation.
1948	18	*for* "quinoid" *read* "quinonoid."
2094	7	,, "colourless" *read* "coloured."
2189	5	,, "  " *read* "  ."

* From bottom.